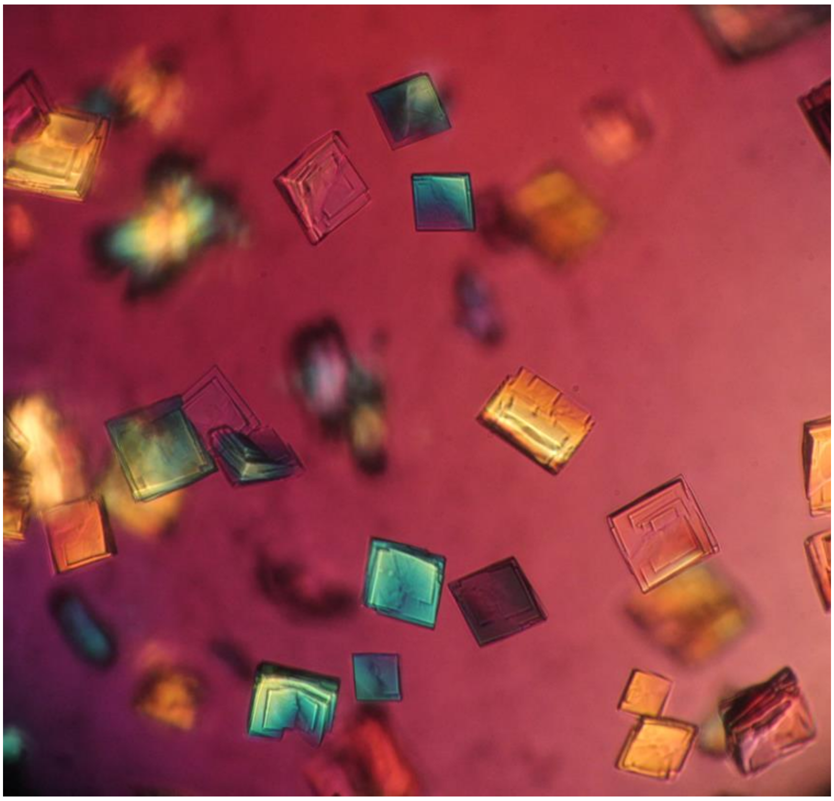
FACET

DACG NewsLetter



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issue 1

FACET
Newsletter of the Dutch Association for Crystal Growth (DACG), section of the KNCV and the NNV.

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DACG board

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Dr. Hugo Meekes (RU)	WWW

Cover figure

Polarized light microscopy picture of F(ab`)2 fragments of a monoclonal antibody crystallized against ammonium sulfate (in HEPES) by vapor diffusion hanging-drop technique. Some crystals appear as an opened book.
Image by Hielke van Splunder; Bachelor thesis, WUR/Synthon Biopharmaceuticals.

From the editor

This year's first issue of the FACET is out.

The DACG fall meeting was held in Wageningen in October. Full coverage is included! The highlight was the presentation of the KNCV Piet Bennema Award for Crystal Growth via a skype connection.

Also, do not forget, the spring symposium is on Friday April 12th in Enschede! Sign in by April 6th, 2019!

As always, it is easy to contribute to the FACET: recently published articles and theses, photos for cover figure, relevant announcements, … Contributions may be delivered by mail, e-mail, or telephone. Your ideas are welcome, please notify the editor: Marketta Uusi-Penttilä

Marketta Uusi-Penttilä

Upcoming events

- DACG Spring Meeting, Friday 12 Apr 2019, University of Twente, Enschede
- DACG Fall Meeting, 4 Oct 2019, Eindhoven (preliminary title: Advances in Electron microscopy for Crystal growth)

- Symposium on the occasion of the 50th anniversary of BACG, 9-11 July 2019, London
- 7th Recrystallization and Grain Grain Growth Conference, 4-9 Aug 2019, Ghent (Belgium)
- ICCGE-19—OMVPE-19, July 28–August 2, 2019, Keystone (Colorado, USA)
- 21st International Symposium on Industrial Crystallization - ISIC21, 8-11 Sep 2020, Potsdam (Germany)

From the board

As you can read from the Annual report of the DACG, published in the previous Facet, the DACG is back in full swing as platform for the crystal growth community in the Netherlands. In the past three years, we have organized two events per year and re-established the Kristalgroeiprijs under a new name: the Piet Bennema Award for Crystal Growth.

To stay in touch with all the research groups studying crystal growth and crystallization, and to support the work of the board, we have built up an academic network of contact persons at Dutch universities. These contact persons help us in collecting news from our community. They keep us informed about new PhD. theses and provide us with contributions for our symposiums and lab visits. You will find our network on the Links page of our internet site.

In line with the new privacy legislation GDPR (General Data Protection Regulation (Dutch AVG)), we have made a privacy statement. It describes how we will use your personal data within our association for the purpose of organizing events, related to crystal growth. You can find the privacy statement on our internet site.

As DACG, we are a section of the KNCV (the Royal Netherlands Chemical Society), as well as the NNV (the Netherlands Physical Society). As board, we are actively in contact with both societies. They help us to get into contact with other sections and invite us to think with them about the future of chemistry and physics in the Netherlands. As a section of the KNCV and NNV, we are quite small, but using their network, we can reach a larger audience than just our community.

Looking forward to 2019, we have already planned our annual events. On Friday, April 12, we will visit the University of Twente for our Spring meeting. Former DACG board member and webmaster Arie van Houselt has taken the lead in organizing this meeting. Traditionally, we give the PhD students from our community the floor to present their research to a broader audience of crystal growers. You will find the program for this symposium in this Facet.
Furthermore, we have planned our Annual meeting, together with a company visit, on Friday, October 4. ThermoFisher Scientific in Eindhoven. More information will come in the next issue of Facet.

Although a lot has been done already, there a still a few things high on our wish list to get done in the coming years. The first is our internetsite, generally considered as “late 20th century”. We could do a better job here, and we are working on it. Hopefully,you will see the results in the course of the year.

A next item on our to-do-list is to get (back) into contact with our sister organizations BACG (UK) and DGKK (Germany). The BACG will celebrate its 50th anniversary in 2019. The DACG will contribute to this event with a lecture by Wim Noorduin (AMOLF, Amsterdam).

As DACG, we celebrate our 50th anniversary in 2022. We started as “Kontaktgroep Kristalgroei Nederland” in 1972 and changed our name to NVKG / DACG in 1998. It is still some years ahead of us, but we have already started thinking how we will celebrate this event. We will keep you informed about our progress.

Looking forward to meeting you all on April 12 on our Spring meeting,

Hans te Nijenhuis,
Chairman DACG

DACG Spring Symposium

University of Twente, Enschede, 12 April 2019

Fundamentals & Applications of Crystal Growth

09:30 – 10:00	**Registration and coffee**
10:00 – 10:15	**Welcome and introduction** Hans te Nijenhuis / Arie van Houselt
10:15 – 11:45	**Germanene: the germanium analogue of graphene** Harold Zandvliet (University of Twente)
10:45 – 11:05	**On the shape of hexagonal boron nitride islands studied with Low Energy Electron Microscopy** Martina Tsvetanova (University of Twente)
11:05 – 11:25	**Ge_2Pt hut clusters: a substrate for germanene** Rik van Bremen (University of Twente)
11:25 – 12:00	**Poster presentation pitches** Presenters of posters
12:00 – 13:15	**Lunch + poster session (1)**
13:15 – 13:35	**Crystal formation of zinc oxide** Mark van Rijt (TU/e)
13:35 – 13:55	**Crystal growth on mica: interface properties** Sander Brugman (RU Nijmegen)
13:55 – 14:15	**Kidney stone formation** Fatma Ibis (TU Delft)
14:15 – 14:35	**High pressure magnetron sputtering of Ge nanoparticles for quantum dot solar cells** Xiaotian Zhu (RUG)
14:35 – 15:00	**Coffee break + poster session (2)**
15:00 – 15:20	**Self-assembly of perovskite microshapes** Lukas Helmbrecht (AMOLF/UvA)
15:20 – 15:40	**Self-assembly of shape-controlled metal chalcogenides** Hans Hendrikse (AMOLF/UvA)
15:40 – 17:00	**Labtour**
17:00 – 18:00	**Drinks / nibbles**

Venue: University of Twente, Waaier 3, Hallenweg 22, 7522 NH, Enschede plattegrond (ingang via hal B)

For registration see next page or visit DACG website.

dutch association for crystal growth
DACG
NVKG
nederlandse vereniging voor kristalgroei

DACG Spring Symposium

University of Twente, Enschede, 12 April 2019

Fundamentals & Applications of Crystal Growth

REGISTRATION FORM

For registration, please complete this form and send the scanned form as an attachment to pintnw@utwente.nl & a.e.d.m.vanderheijden@tudelft.nl, ultimately **by 6 April 2019**.

The symposium fee (including coffee, lunch and drinks) is:

25 EURO for students and DACG members
40 EURO for non-members (you will be offered to be enrolled as a DACG member in 2019)

Payment of symposium fee **preferably by bank transfer**:
Nederlandse Vereniging van Kristal Groei
NL 60 INGB 0004305158

Another possibility is cash payment at the symposium.

Name (first name and surname):
E-mail:
Affiliation:
Postal address:
Postal code:
City:

Member DACG / (PhD-)student / None of the two *(delete what is not applicable)*

Dietary requirements for lunch:

Poster (including 2 minute poster pitch): yes/no
Title:

For details regarding DACG privacy policy see our website.

DACG Fall Symposium and Annual meeting

WUR, Wageningen, October 3, 2018

On October 3, 2018, the DACG organized its Annual Meeting and Symposium, hosted by **Renata van der Weijden**, Wageningen University & Research. The theme of the symposium was "Biomineralization". **Hans te Nijenhuis** (president DACG) and **Cees Buisman** (WUR) welcomed the almost 40 participants. This was followed by a Keynote lecture by **Jan Weijma** (WUR) giving an overview of biocrystallization for resource recovery and environmental protection. The topic "controlling properties of sulfur particles formed in biological gas desulfurization" was explained by **Annemerel Mol** (WUR/WETSUS). Just before lunch the DACG members convened for their DACG Annual Meeting. Other participants had the opportunity to take a guided labtour, including a short presentation by **Yang Lei** on the influence of cell configuration and long-term operation on electrochemical phosphorus recovery.

Jan Weijma

Annemerel Mol

Ricardo Cunha

Mani Diba

Giulia Mirabello

Ricardo Cunha (WUR/WETSUS) continued after lunch with a presentation on anaerobic calcium phosphate biogranulation. The last two presentation were from TU Eindhoven: **Mani Diba** spoke about exploiting bisphosphonate-bioactive glass interactions for development of bone regenerative biomaterials and **Giulia Mirabello** presented her results on crystallization by particle attachment from a colloidal assembly process perspective. Each of the presentations ended with a lively scientific discussion.

From left to right: Simon Hageman, Hans te Nijenhuis, Wester de Poel, Tom Leyssens and Paul Verwer; on the screen at the back (via Skype): Paul Smeets.

Nico Sommerdijk

After a coffee break, the prize winner **Paul Smeets** (TU/e) of the KNCV Piet Bennema Award for Crystal Growth was announced by **Tom Leyssens**, chairman of the jury, which further consisted of **Herman Kramer** and **Paul Verwer**. Paul Smeets, living and working in the USA, witnessed this part of the symposium via Skype. Certificates with an Honorable Mention were handed out to the other two scientists **Wester de Poel** (RUN) and **Simon Hageman** (WUR) that were nominated for this award. Finally, **Nico Sommerdijk** (TU/e) presented the results of the PhD study of Paul Smeets on pathway complexity in $CaCO_3$ crystallization. The symposium closed with an informal get-together and drinks.

The DACG Spring Meeting was attended by 42 participants, of which 34 from university and 8 from industry. We kindly acknowledge the hospitality of WUR and especially Renata van der Weijden for hosting the DACG annual meeting.

Antoine van der Heijden

Membership

Becoming a member of the DACG is easy: send an e-mail message to Antoine van der Heijden.

The annual membership fee in 2018 is € 15 for professionals, € 10 for retired people and € 5 for (PhD) students.

Participating in one of the biannual symposia for the first time automatically includes a membership for one year.

Recent publications

- Teng Li, Hanglong Wu, Johannes Ihli, Zhiqiang Ma, Frank Krumeich, Paul H. H. Bomans, Nico A. J. M. Sommerdijk, Heiner Friedrich, Joseph P. Patterson and Jeroen A. van Bokhoven, Cryo-TEM and electron tomography reveal leaching-induced pore formation in ZSM-5 zeolite, *J. Mater. Chem. A*, **7** (2019), 1442-1446.

  Affiliations:
  - ETH Zurich, Department of Chemistry and Applied Bioscience, Institute for Chemical and Bioengineering, Zurich, Switzerland (Li, Ma, Krumeich, Bokhoven)
  - Eindhoven University of Technology, Laboratory of Materials and Interface Chemistry, Center of Multiscale Electron Microscope, Eindhoven, The Netherlands (Wu, Bomans, Sommerdijk, Friedrich, Patterson)
  - Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, The Netherlands (Wu, Bomans, Sommerdijk, Friedrich, Patterson)
  - Paul Scherrer Institute, Villigen, Switzerland (Ihli, Bokhoven)

  Zeolites are the catalytic workhorses of the refinery and chemicals production industry. Their inherent micropores lead to remarkable shape-selectivity, but also present diffusion limitations on reactions. One scalable approach to further their functionality is to introduce mesopores into the individual zeolite crystal by base leaching. Using cryogenic transmission electron microscopy (cryo-TEM), we are able to capture the pore formation process in ZSM-5 zeolites in the solution state, first forming mesopores, to eventually yielding hollow crystals. Electron tomography indicates that the larger pores in the initial leaching stages tend to exist at the boundary between the aluminum-rich shell and the aluminum-poor core, while multiple small pores are also present within the aluminum-poor core. This indicates that pore formation is based on crystalline and chemical inhomogeneities at the single crystal level.

- Yifei Xu, Nico A. J. M. Sommerdijk, Aragonite formation in confinements: A step toward understanding polymorph control, *PNAS*, **115** (2018), 8469-8471.

  Affiliations:
  - Laboratory of Materials and Interface Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands (Xu, Sommerdijk)
  - Center for Multiscale Electron Microscopy, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands (Xu, Sommerdijk)
  - Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, The Netherlands (Xu, Sommerdijk)

  [No abstract available]

- Cunha, J.R., Tervahauta, T., van der Weijden, R.D., Hernández Leal, L., Zeeman, G., Buisman, C.J.N., Simultaneous recovery of calcium phosphate granules and methane in anaerobic treatment of black water: Effect of bicarbonate and calcium fluctuations, *J. Environ. Manage.* **216** (2017), 399–405.

  Affiliations:
  - Wetsus, European Centre of Excellence for Sustainable Water Technology, Leeuwarden, The Netherlands (Cunha, Tervahauta, Leal, Buisman)
  - Sub-department of Environmental Technology, Wageningen University, Wageningen, The Netherlands (Cunha, van der Weijden, Zeeman, Buisman)

  Calcium phosphate (CaP) granules were discovered in the anaerobic treatment of vacuum collected black water (BW), using upflow anaerobic sludge blanket (UASB) technology. This allows simultaneous recovery of CaP granules and methane in the UASB reactor. However, the role of BW composition on CaP granulation is not yet understood. Moreover, CaP granulation was not observed in previous research on anaerobic treatment of BW, although similar treatment conditions were applied. Therefore, this study shows specifically the influence of bicarbonate and calcium fluctuations in BW on the phosphorus accumulation in the UASB reactor, which directly affects CaP granulation. Without calcium addition, 5% of the total phosphorus (P) fed was found as CaP granules in the reactor (61 mgP g^{-1}dried matter), after 260 days of operation. Simultaneously, 65% of the COD in BW was efficiently converted into methane at 25 °C. Variations of bicarbonate and calcium concentrations in raw BW showed a significant influence on phosphorus accumulation in the UASB reactor. Geochemical modelling showed that the increase of soluble calcium from 39 to 54 mg L^{-1} in BW triggers supersaturation for calcium phosphate precursors ($Ca_x(PO_4)_y$). Concurrently, bicarbonate decreased from 2.7 to 1.2 g L^{-1}, increasing further the ionic activity of calcium. Formation and accumulation of seed particles possibly enhanced CaP granulation. Preliminary results showed that addition of calcium (Ca^{2+}/PO_4^{3-} molar ratio of 3) increased the accumulation of total P in the UASB reactor to more than 85%. This further increases the granulation rate and consequently, the process feasibility.

- Cunha, J.R., Schott, C., van der Weijden, R.D., Leal, L.H., Zeeman, G., Buisman, C, Calcium addition to increase the production of phosphate granules in anaerobic treatment of black water, *Water Res.,* **130** (2018), 333-342.

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  - Wetsus, European Centre of Excellence for Sustainable Water Technology, Leeuwarden, The Netherlands (Cunha, Schott, Leal, Buisman)
  - Sub-department of Environmental Technology, Wageningen University, Wageningen, The Netherlands (Cunha, van der Weijden, Zeeman, Buisman)

  Simultaneous recovery of calcium phosphate granules (CaP granules) and methane from vacuum collected black water (BW), using an upflow anaerobic sludge blanket (UASB) reactor was previously investigated. It was calculated that only 2% of the total phosphorus (P) fed was present as CaP granules whereas 51% of the P accumulated dispersed in the reactor, limiting the applicability of this process for recovery of phosphate. This study proposes adding calcium to increase the P accumulation in the reactor and the production of CaP granules. Calcium was added in a lab-scale UASB reactor fed with BW. An identical UASB reactor was used as reference, to which no calcium was added. The treatment performance was evaluated by weekly monitoring of influent, effluent and produced biogas. Sludge bed development and CaP granulation were assessed through particle size analysis. The composition and structure of CaP granules were chemically and optically assessed. Calcium addition increased accumulation of P in the reactor and formation and growth of granules with size > 0.4 mm diameter (CaP granules). Moreover, with calcium addition, CaP granules contained 5.6 ± 1.5 wt% of P, while without calcium a lower P content was observed (3.7 ± 0.3 wt%). By adding Ca, 89% of the incoming P from BW accumulated in the reactor and 31% was sampled as CaP granules (> 0.4 mm diameter). Addition of 250 mgCa L−1 of BW was the optimum loading found in this study. Furthermore, no significant reduction in CODTotal removal (> 80%) and CH4 production (0.47 ± 0.10 gCOD-CH4 g−1CODTotal-BW) was observed. Therefore, adding calcium can significantly increase the CaP granulation without inhibiting the simultaneous CH4 recovery. This further indicates the potential of this process for phosphate recovery.

- Cunha, J.R., Tervahauta, T., Van Der Weijden, R.D., Temmink, H., Hernández Leal, L., Zeeman, G., Buisman, C.J.N., The Effect of Bioinduced Increased pH on the Enrichment of Calcium Phosphate in Granules during Anaerobic Treatment of Black Water, *Environ. Sci. Technol.,* **52** (2018), 13144–13154.

Affiliations:

  - Wetsus, European Centre of Excellence for Sustainable Water Technology, Leeuwarden, The Netherlands (Cunha, Tervahauta, Van Der Weijden, Temmink, Leal, Buisman)
  - Sub-department of Environmental Technology, Wageningen University, Wageningen, The Netherlands (Cunha, Van Der Weijden, Temmink, Zeeman, Buisman)

Simultaneous recovery of calcium phosphate granules (CaP granules) and methane in anaerobic treatment of source separated black water (BW) has been previously demonstrated. The exact mechanism behind the accumulation of calcium phosphate ($Ca_x(PO_4)_y$) in CaP granules during black water treatment was investigated in this study by examination of the interface between the outer anaerobic biofilm and the core of CaP granules. A key factor in this process is the pH profile in CaP granules, which increases from the edge (7.4) to the center (7.9). The pH increase enhances supersaturation for $Ca_x(PO_4)_y$ phases, creating internal conditions preferable for $Ca_x(PO_4)_y$ precipitation. The pH profile can be explained by measured bioconversion of acetate and H_2, HCO_3^- and H^+ into CH_4 in the outer biofilm and eventual stripping of CO_2 and CH_4 (biogas) from the granule. Phosphorus content and $Ca_x(PO_4)_y$ crystal mass quantity in the granules positively correlated with the granule size, in the reactor without Ca^{2+} addition, indicating that the phosphorus rich core matures with the granule growth. Adding Ca^{2+} increased the overall phosphorus content in granules >0.4 mm diameter, but not in fine particles (<0.4 mm). Additionally, H^+ released from aqueous phosphate species during $Ca_x(PO_4)_y$ crystallization were buffered by internal hydrogenotrophic methanogenesis and stripping of biogas from the granule. These insights into the formation and growth of CaP granules are important for process optimization, enabling simultaneous $Ca_x(PO_4)_y$ and CH_4 recovery in a single reactor. Moreover, the biological induction of $Ca_x(PO_4)_y$ crystallization resulting from biological increase of pH is relevant for stimulation and control of (bio)crystallization and (bio)mineralization in real environmental conditions.

- Cunha, J.R., Morais S., Silva, J.C., van der Weijden, R., Hernandez Leal, L., Zeeman, G., Buisman, C.J.N., Bulk pH and carbon source are key factors for calcium phosphate granulation, *Environ. Sci. Technol.*, (2019), Just Accepted Manuscript.

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  - Sub-department of Environmental Technology, Wageningen University, Wageningen, The Netherlands (Van Der Weijden, Temmink, Zeeman, Buisman)
  - Department of Chemical Engineering, Faculty of Engineering of the University of Porto (FEUP), Porto, Portugal (Morais, Silva)

  Recovery of calcium phosphate granules (CaP granules) from high-strength wastewater is an opportunity to reduce the natural phosphorus (P) scarcity, geographic imbalances of P reserves, and eutrophication. Formation of CaP granules was previously observed in an upflow anaerobic sludge bed (UASB) reactor treating source separated black water and is enhanced by Ca^{2+} addition. However, the required operating conditions and influent composition for CaP granulation are still unknown. In this study, we have experimentally demonstrated that the carbon source and bulk pH are crucial parameters for the formation and growth of CaP granules in a UASB reactor, operating at relatively low upflow velocity (<1 cm h^{-1}). Degradation of glucose yielded sufficient biomass (microbial cells and extracellular biopolymers) to cover crystal and amorphous calcium phosphate [$Ca_x(PO_4)_y$], forming CaP granules. Influent only containing volatile fatty acids as the carbon source did not generate CaP granules. Moreover, bulk pH between 7.0 and 7.5 was crucial for the enrichment of $Ca_x(PO_4)_y$ in the granules over bulk precipitation. Bulk pH 8 reduced the $Ca_x(PO_4)_y$ enrichment in granules of >1.4 mm diameter from 9 to 5 wt % P. Moreover, for bulk pH 7.5, co-precipitation of $CaCO_3$ with $Ca_x(PO_4)_y$ was reduced.

- Lei, Yang, Bingnan Song, Michel Saakes, Renata D. van der Weijden, and Cees JN Buisman, Interaction of calcium, phosphorus and natural organic matter in electrochemical recovery of phosphate, *Water research,* **142** (2018), 10-17.

  Affiliations:
  - Wetsus, European Centre of Excellence for Sustainable Water Technology, Leeuwarden, The Netherlands (Cunha, Saakes, Van Der Weijden, Leal, Buisman)
  - Sub-department of Environmental Technology, Wageningen University, Wageningen, The Netherlands (Cunha, Song, Van Der Weijden, Buisman)

  To address the issues of eutrophication and the potential risk of phosphorus (P) shortage, it is essential to remove and recover P from P-containing streams to close this nutrient cycle. Electrochemical induced calcium phosphate (CaP) precipitation was shown to be an efficient method for P recovery. However, the influence of natural organic matter (NOM) is not known for this treatment. In this paper, the behavior of NOM and its effect on CaP precipitation was studied. In contrast to studies where NOM hindered CaP precipitation, results show that the interaction of NOM with CaP improves the removal of P, independent of the types of NOM. The P removal at the average increased from 43.8 ± 4.9% to 58.5 ± 1.2% in the presence of 1.0 mg L^{-1} NOM. Based on the yellow color of the CaP product, NOM is co-precipitated. The bulk solution pH with and without buffers has totally different effects on the precipitation process. Without buffer, CaP precipitates on the cathode surface in a wide pH range (pH 4.0–10.0). However, the precipitation process is completely inhibited when the bulk solution is buffered at pH 4.0 and 6.0. This is probably due to neutralization of OH^- by the buffers. Regardless of the presence or absence of NOM and solution pH, the recovered products are mainly amorphous CaP unless the electrolysis time was increased to seven days with 4.0 A m^{-2}, in which crystalline CaP formed. These findings advance our understanding on the interaction of Ca, P and NOM species for the application of electrochemical method for P recovery from real wastewater.

- Yang Lei, Jorrit Christiaan Remmers, Michel Saakes, Renata D. van der Weijden, and Cees JN Buisman, Is There a Precipitation Sequence in Municipal Wastewater Induced by Electrolysis?, *Environ. Sci. Technol.,* **52** (2018), 8399-8407.

  Affiliations:
  - Wetsus, European Centre of Excellence for Sustainable Water Technology, Leeuwarden, The Netherlands (Lei, Saakes, Van Der Weijden, Buisman)
  - Sub-department of Environmental Technology, Wageningen University, Wageningen, The Netherlands (Lei, Remmers, Van Der Weijden, Buisman)

Electrochemical wastewater treatment can induce calcium phosphate precipitation on the cathode surface. This provides a simple yet efficient way for extracting phosphorus from municipal wastewater without dosing chemicals. However, the precipitation of amorphous calcium phosphate (ACP) is accompanied by the precipitation of calcite ($CaCO_3$) and brucite ($Mg(OH)_2$). To increase the content of ACP in the products, it is essential to understand the precipitation sequence of ACP, calcite, and brucite in electrochemical wastewater treatment. Given the fact that calcium phosphate (i.e., hydroxyapatite) has the lowest thermodynamic solubility product and highest saturation index in the wastewater, it has the potential to precipitate first. However, this is not observed in electrochemical phosphate recovery from raw wastewater, which is probably because of the very high Ca/P molar ratio (7.5) and high bicarbonate concentration in the wastewater resulting in formation of calcite. In the case of decreased Ca/P molar ratio (1.77) by spiking external phosphate, most of the removed Ca in the wastewater was used for ACP formation instead of calcite. The formation of of brucite, however, was only affected when the current density was decreased or the size of cathode was changed. Overall, the removal of Ca and Mg is much more affected by current density than the surface area of cathode, whereas for P removal, the reverse is true. Because of these dependencies, though there is no definite precipitation sequence among ACP, calcite, and brucite, it is still possible to influence the precipitation degree of these species by relatively low current density and high surface area or by targeting phosphorus-rich wastewaters.

- Yang Lei, Michel Saakes, Renata D. van der Weijden, and Cees JN Buisman, Effects of current density, bicarbonate and humic acid on electrochemical induced calcium phosphate precipitation, *Chemical Engineering Journal,* **342** (2018), 350-356.

  Affiliations:
  - Wetsus, European Centre of Excellence for Sustainable Water Technology, Leeuwarden, The Netherlands (Lei, Saakes, Van Der Weijden, Buisman)
  - Sub-department of Environmental Technology, Wageningen University, Wageningen, The Netherlands (Lei, Van Der Weijden, Buisman))

  Phosphorus (P) removal and recovery from sewage as calcium phosphate (CaP) by chemical precipitation is a widely used method. To avoid the addition of chemicals to increase the pH of the bulk solution and the need for a further separation step in conventional chemical precipitation process, we developed an electrochemical method, which can locally increase the pH near a Ti cathode. The separation of product and liquid then happens simultaneously by accumulating CaP at the electrode surface. The current density plays a crucial role in this system. A current density of 19 A/m^2 results in the formation of crystalline CaP rather than amorphous CaP, but it does not enhance the removal of P in 24 h. Moreover, the current efficiency decreases with increasing current density. Furthermore, the increased H_2 production at high current density may push the precipitated CaP back to the bulk solution, resulting in its dissolution. In the presence of bicarbonate (1–5 mM) or humic acid (1–20 mg/L), the removal of P was higher. This is probably due to the inhibited CaP precipitation in the bulk solution which in turn leaves more Ca and P ions available for the local precipitation on the cathode. However, bicarbonate at high concentration (10 mM) dropped P removal from 52 to 25%. This is caused by competition of carbonate and phosphate with the free Ca^{2+} ions and also by buffering the producted hydroxide ions at the cathode. The study shows that P can be removed as CaP by electrochemical precipitation at low current densities at common concentrations of bicarbonate and humic acid.

- N.A. Garcia , P. Raiteri, E. Vlieg and J.D. Gale,
  Water Structure, Dynamics and Ion Adsorption at the Aqueous {010} Brushite Surface, *Minerals*, **8** (2018), 334.

  Affiliations
  - Curtin Institute for Computation/The Institute for Geoscience Research (TIGeR), School of Molecular and Life Sciences, Curtin University, P.O. Box U1987, Perth, WA 6845, Australia
  - Institute for Molecules and Materials, Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

  Understanding the growth processes of calcium phosphate minerals in aqueous environments has implications for both health and geology. Brushite, in particular, is a component of certain kidney stones and is used as a bone implant coating. Understanding the water–brushite interface at the molecular scale will help inform the control of its growth. Liquid-ordering and the rates of water exchange at the brushite–solution interface have been examined through the use of molecular dynamics simulation and the results compared to surface X-ray diffraction data. This comparison highlights discrepancies between the two sets of results, regardless of whether force field or first principles methods are used in the simulations, or the extent of water coverage. In order to probe other possible reasons for this difference, the free energies for the adsorption of several ions on brushite were computed. Given the exothermic nature found in some cases, it is possible that the discrepancy in the surface electron density may be caused by adsorption of excess ions.

- A.h.J. Engwerda, J.C.J. Mertens, P. Tinnemans, H. Meekes, F.P.J.T. Rutjes and E. Vlieg, Solid-Phase Conversion of Four Stereoisomers into a Single Enantiomer, *Angewandte Chemie-International Edition*, **57** (2018), 15441-15444.

  Affiliation
  - Institute for Molecules and Materials, Radboud University, Heyendaalseweg 135, 6525AJ Nijmegen, The Netherlands

  Viedma ripening is an emerging method for the solid-phase deracemization of mixtures of enantiomers. Up to now, the scope of the method has remained limited to molecules with a single stereocenter. We show here that this method can be extended to obtain a single enantiomer from a mixture of stereoisomers with two different stereocenters. In addition, we show that by using tailor-made chiral additives, the conversion time can be reduced by a factor of 100.

- G. Belletti, H. Meekes, F.P.J.T. Rutjes and E. Vlieg, Role of Additives during Deracemization Using Temperature Cycling, *Crystal Growth & Design*, **18** (2018), 6617-6620.

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  Temperature cycling, alongside Viedma ripening, has been established as a reliable method for deracemizing racemic mixtures of chiral compounds that crystallize as a conglomerate. Here we report that the speed of temperature cycling can be increased by using chiral additives. We also demonstrate that the chirality of the additive determines the final enantiomeric state of the solid phase. Viedma ripening experiments using equivalent conditions, with and without chiral additives, are always found to be slower.

- W. de Poel, J.A.A.W. Elemans, W.J.P. van Enckevort, A.E. Rowand and E. Vlieg, Epitaxial crystallization of insulin on an ordered 2D-polymer template, *Chem. Eur. J.* DOI: 10.1002/chem.201805276
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  2-Dimensional Polymers (2DP) are a novel class of material that consist of a monolayer of ordered molecular building blocks, that have been covalently linked. One of these monomers was self-assembled on a flat muscovite mica scaffold and subsequently the organic layer was polymerized. The resulting flat and stable 2DP layer was used as a template for protein crystallization. Crystals of insulin were epitaxially grown on the template, while insulin crystals grown on clean muscovite mica had a random orientation. The template was selective, since no epitaxially ordered crystals were formed of hen egg white lysozyme, bovine serum albumin, or talin.

- C. Bernades, M. Carravetta, S. J. Coles, E. R. H. van Eck, H. Meekes, M. E. Minas da Piedade, M. B. Pitak, M. Podmore, T. A. H. de Ruiter, L.-C. Sögütoglu, R.R.E. Steendam and T. Threlfall. The curious case of acetaldehyde phenylhydrazone: Resolution of a 120 year old puzzle where forms with vastly different melting points have the same structure, *Cryst. Growth. Des.*, 19 (2019), 907–917

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The solid forms of acetaldehyde phenylhydrazone were investigated in detail over a century ago, with curious results: it was reported that a low melting form could be transformed into a high melting form by trace alkali, and the reverse process could be brought about with trace acid. Our reinvestigation of this puzzle with modern instrumentation has shown that all samples, although exhibiting sharp melting points varying from 56 to 101 °C, have identical IR and solid-state NMR spectra and identical crystal structures. NMR studies of the melts provided the key to the understanding of this strange behavior: differently melting samples did so because they initially melted to liquids with different proportions of the Z and E isomers, although given enough time they all tended to the same equilibrium proportion. The leading role of the isomerization rate in the melt was confirmed in cyclic differential scanning calorimetry experiments and accompanying simulations. In the case of polymorphism, different structures melt to the same liquid. In the present case, the same structure melts to different liquids.

- H.M. Cuppen , M.M.H. Smets, A.M. Krieger, J.A. van den Ende, H. Meekes, E.R.H. van Eck, and C.H. Görbitz, The Rich Solid-State Phase Behavior of l-Phenylalanine: Disappearing Polymorphs and High Temperature Forms, **19** (2019), DOI: 10.1021/acs.cgd.8b01655

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  - Department of Chemistry, University of Oslo, N-0315 Oslo, Norway

After years of controversy over the solid state structure of the essential amino acid l-phenylalanine, four different polymorphic forms were published recently. The common form I has symmetry P21 with four molecules in the asymmetric unit (Z′ = 4), similar to form III, but with a different arrangement of molecular bilayers. Form II, obtained from the hydrate at very low humidity, is unrelated to forms I and III, as is the high-density form IV. The present investigation demonstrates that this prototype aromatic amino acid has two additional high-temperature phases Ih and IIIh obtained from form I and form III above 458 and 440 K, respectively, when flipping between two alternative side-chain conformations becomes dynamic and causes pairs of molecules, initially crystallographically independent, to become equivalent above a sharp transition temperature. These abrupt and reversible phase changes occur with a reduction of Z′ from 4 (low T) to 2 (high T) and modified crystal symmetry. We furthermore experienced an example of disappearing polymorph for form I which after growing form III in one of our laboratories could no longer be crystallized at room temperature. In contrast, form III crystals may be irreversibly converted to form I crystals as a result of sliding of molecular bilayers in the crystal at elevated temperature. No conversions between the high-temperature forms Ih and IIIh were found. The remarkable crystallographic results are here corroborated by Molecular Dynamics and metadynamics simulations of the form I – form III system.

- A. H. J. Engwerda, R. Maassen, P. Tinnemans, H. Meekes, F. P. J. T. Rutjes and E. Vlieg, Attrition-Enhanced Deracemization of the Antimalaria Drug Mefloquine, *Angewandte Chemie Int. Ed.*, **58** (2019), 1670-1673.

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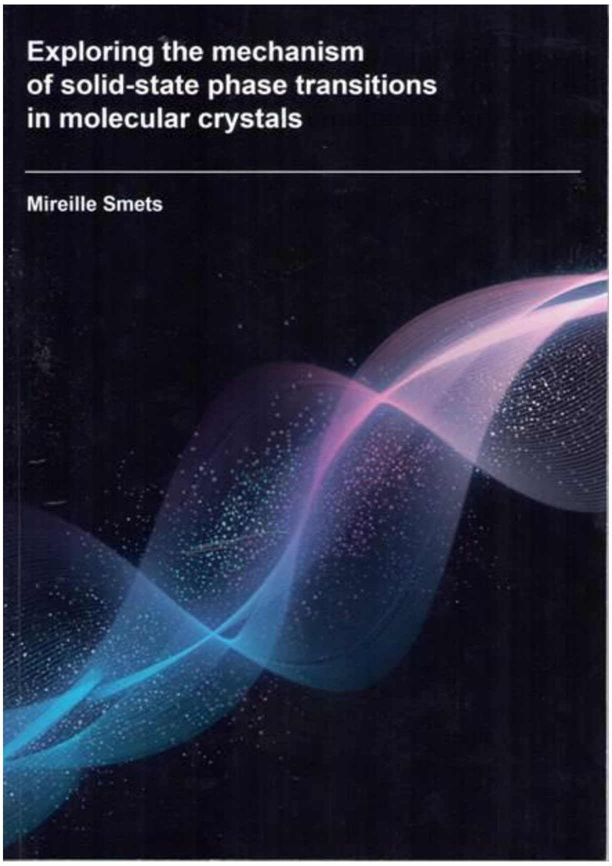
  Mefloquine is an important drug for prevention and treatment of malaria. It is commercially available as a racemic mixture, wherein only one enantiomer is active gainst malaria, while the other one causes severe psychotropic effects. By converting the drug into a compound that crystallizes as a racemizable racemic conglomerate, the deracemization of mefloquine into the desired enantiomer was achieved.

PhD theses

- Mireille Smets, Exploring the mechanism of solid-state phase transitions in molecular crystals
  PhD defense: 28 September 2018, Radboud Universiteit, Nijmegen

  Promotors: Prof.dr. H.M. Cuppen and Prof.dr. E. Vlieg
  Co-promotors: Dr. H. Meekes and Dr. E.R.H. van Eck



Polymorphism is the ability of a compound to crystallise in more than one crystal structure. When a polymorphic form of a compound is not the stable form at a certain temperature and pressure, solid-state phase transitions can occur. The mechanism of solid-state phase transitions has been under much debate, but the nucleation-and-growth theory of Mnyukh is mostly accepted by the community. However, in case the two polymorphic forms involved have similar crystal structures, there is an ongoing debate if the phase transition mechanism could involve cooperative motion of molecules. The term 'cooperative motion' is used in this work for the simultaneous movement of multiple neighbouring molecules, on a limited length scale of tens to a few hundreds of molecules. This is different from cooperative motion in second-order phase transitions with an infinite correlation length. This work describes the study of the solid-state phase transitions of linear amino acids as a model system for molecular crystals that can involve cooperative motion. These amino acids have similar crystal structures and reversible single-crystal-to-single-crystal phase transitions. Therefore, this thesis contributes to the understanding of the mechanism of these solid-state phase transitions on a molecular scale.

- Giulia Mirabello, Nucleation and growth of magnetite in bioinspired environments
  PhD defense: 17 October 2018, TU Eindhoven

  Promotor: Prof.dr. N.A.J.M. Sommerdijk
  Promotor: Prof.dr. G. de With
  Copromotor: Dr. H. Friedrich

  Groundwater represents an important resource of water and contains various naturally dissolved ions. In order to use groundwater as potable water these ions need to be removed according to many health guide lines. Particularly important is the removal of iron as its presence above the recommended level (< 0.3 mg/L) can affect the appearance, the taste and the smell of the water. Typically the total Fe concentration in groundwater is in the range from 1-50 mg/L. Since groundwater naturally is kept under anaerobic conditions, iron is present in the Fe^{2+} oxidation state. Currently, Fe is removed by oxidation/filtration, where the Fe^{2+} is first oxidized and then precipitated as ferric (oxy)hydroxide. The ferric sludge produced from the filtration step is highly hydrated and metastable. Production of iron oxide nanoparticles instead of this sludge would give many advantages as such a product can be used for other applications, thereby reducing the costs for transportation and disposal. Magnetite, Fe_3O_4, is the most interesting of iron oxide known in terms of its properties and future applications.

  This thesis concentrated on finding suitable chemical methods to produce magnetite nanoparticles under aqueous and ambient condition to be used during the Fe removal process in groundwater. By taking inspiration from nature different precursor-based approaches were designed and explored to produce controlled magnetite crystals. Particular attention was given to the study of the magnetite formation mechanism to improve our understanding of the Fe chemistry and to obtain better synthetic control.

  The results show that the use of poorly crystalline precursor phases helps in controlling the supersaturation of Fe. The precursor phase acts as a reservoir of Fe ions stored in a metastable mineral phase thereby preventing precipitation of unwanted iron oxide phases. Furthermore, the investigation on the formation mechanism suggests that Fe_3O_4forms by a particle attachment (CPA) mechanism, regardless the synthetic method used, and therefore the precursor phase is involved in the process. In fact, the formation of ~ 2 nm primary particles was observed from ferrous (Chapter 4 and 5), ferric (chapter 6), and mixed valence precursor phases (Chapter 3), that later aggregate to form the final magnetite crystals. The synthesis of stable primary particles and the understanding of the exact conditions that control their aggregation represents potentially the key to control magnetite crystallization, an aspect that we have explored in chapter 4 and 6 of this thesis. The preferred formation and aggregation of primary particles can be explained by considering the low solubility of both Fe_{2+} and Fe_{3+} at alkaline pH. Thus, Fe is very unlikely to be found as free ions in solution at this condition and prefers to form particles with a specific chemical composition, possibly close to the one of magnetite. These particles are stable enough to prevent their growth but still sufficiently unstable such as to promote their aggregation and their further conversion into magnetite crystals.

  The understanding gained in this study on magnetite formation can be used to explore the formation of magnetite from groundwater to find alternative methods to remove Fe or to convert the side products produced during the filtration step.

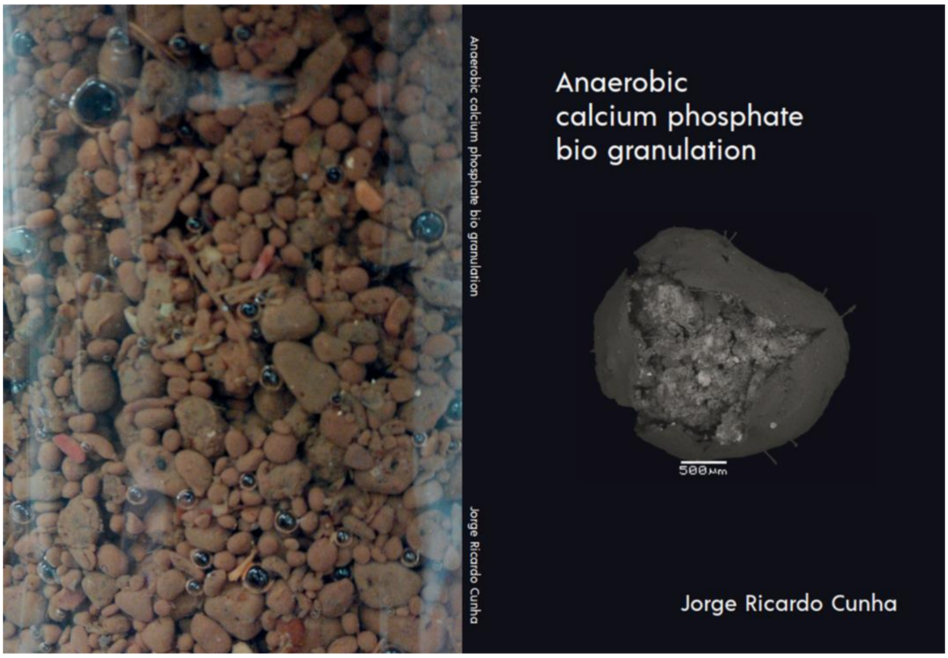
- Weiwei Li, Novel Crystallization Techniques for Separation in Multi-component Systems
  PhD defense: 14 November 2018, TU Delft

  Promotor: Prof.dr.ir. A. Stankiewicz
  Promotor: Prof.dr. J.H. ter Horst
  Copromotor: Dr.ir. H.J.M. Kramer

  Crystallization-based chiral resolution techniques was born when Pasteur discovered the chirality of tartaric acid and manually separated its two enantiopure crystals by his tweezers. Ever since then, these techniques have been in constant development, mainly due to the needs from the pharmaceutical and food industries. In the past decades, techniques such as preferential crystallization have been studied and some of them have already been applied at pilot scale. Deracemization is of more recent date and is actually the process that stirs up attention in chiral resolution the last few years. These techniques draw more and more attention from both academic world and the industries owing to one common feature: the potential to recover the desired enantiomer with unrivaled high product purity in a single process step.

- Ricardo Cunha, Anaerobic calcium phosphate bio granulation
  PhD defense: 30 November 2018, WUR/WETSUS, Wageningen

  Promotor Prof.dr.ir. G Zeeman
  Promotor Prof.dr.ir. CJN Buisman
  Co-promotor Dr. RD van der Weijden



Ricardo Macedo Da Cunha defended his dissertation “ Anaerobic calcium phosphate biogranulation” successfully on November 30th 2018 for his doctors degree from Wageningen University. He carried out his research at Wetsus on the production of calciumphosphate granules from Black Water (from vacuum toilets). These granules are produced in a bioreactor used for methane production. Da Cunha studied the mechanism of formation meticulously and creatively. Based on his insight in the mechanism, he was able to optimize the process for phosphate removal. The produced calciumphosphate can be reused as, or in, fertilizer in agriculture. Recovery of nutrients and making new products from wastewater in an environmentally friendly way are two of the research program themes of Wetsus.

- Ton Engwerda, Deracemization on the edge of stability
  PhD defense: 14 February 2019, Radboud Universiteit, Nijmegen

  Promotors: Prof.dr. E. Vlieg and Prof.dr. F.P.J.T. Rutjes
  Co-promotor: Dr. H. Meekes

Many important compounds, including most drugs, are composed of chiral molecules. This implies that these compounds exist in two forms, which are each other’s mirror image. Though this may seem a marginal difference, the effect of two such mirror images can be very different. For example, in the case of a drug molecule, one molecule can have the desired effect whereas its mirror image causes severe side effects. In this thesis, the conversion of a compound of two mirror images into a single one is researched. This is achieved by grinding a suspension of crystals of the chiral compound, a process known as Viedma ripening. This was performed for several classes of compounds, as well as for the important anti-malaria drug Mefloquine (Lariam). Whereas this process is normally limited to 10% of all molecules, several tricks were employed to achieve the same result for molecules that belong to the other 90%.