ESF / EuroCLIMATE-EuroMinSci - ESRF Workshop

"Environmental Proxies:
From Inorganic Precipitation to Biocrystallization"

30-31 October 2006, ESRF, Grenoble, France

-Scientific report-

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1) Workshop details

Four on-going ***ESF*** projects are dealing with calcareous crystals, sedimentary or biogenic. Two of them belong to the **EuroCLIMATE** Program (***PaleoSalt*** and ***Casiopeia***) and two others to the **EuroMinScI** (***BioCalc*** and ***Cubcat***).

Either studying natural materials (biogenic or chemically produced) or dealing with crystals resulting from experiments, these projects are sharing a common objective: to improve our understanding of the relationships between the crystal structures, their chemical or isotopic compositions and the properties of their growth environments.

An additional characteristic of the naturally produced calcareous crystals is the impact of organic components on their nucleation and growth. Such an influence is obvious for biogenic crystals that are always produced under control of specifically secreted macromolecules. However, crystals freely growing in sea water are also submitted to influence of dissolved or particulate organic compounds that interact with mineral surfaces and may modify the structural and chemical properties. In both cases, consequences of this organo-mineral interplay must be established and interpreted.

This 2-day workshop gathered members of these four projects and some leading scientists in the domain. It provided opportunities for an intensive exchange of information between investigators facing questions that require accurate knowledge of the methods that allow the fine-scale patterns of these organo-mineral composites to be characterized. Owing to the increasing role of synchrotron radiation based methods, ESRF, was a relevant site for such a meeting.

Venue:

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Local organisation was provided by ESRF scientist Jean Susini and assisted by Myriam Dhez The local organizers not only provided the attendees with accomodation, perfect working conditions and catering but they contributed significantly to the success of the meeting itself by i) presenting the ESRF analytical facilities relevant to the meeting topic (J. Susini and Ch. Riekel), and by ii) Encouraging the attendees to use the analytical facilities of several synchrotron beam lines.

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The programme

MONDAY OCTOBER 30th		
08:30-09:00	**Registration**	
09:00-09:15	**Welcome by William Stirling,** Director General of the ESRF	
09:15-09:25	**Opening of the workshop**	**Bernard Avril** European Science Foundation
09:25-10:10	Presentation of the four ESF EuroCLIMATE / EuroMinScI projects	**Jelle Bijma, Anton Eisenhauer, Laurent Charlet, Jean-Pierre Cuif**
Organic and Inorganic Precipitations		
10:10-10:40	The Role of mineral-water interfaces on trace element uptake by calcite: experimental observations in model systems	**Richard J. Reeder** Stony Brook University, Stony Brook, USA
10:40-11:10	***Coffee break***	
11:10-11:40	Calcite precipitation from aqueous solution: Transformation from vaterite and role of solution stoechiometry	**Gernot Nehrke** AWI, Bremerhaven, Germany
Synchrotron Based Methods		
11:40-12:10	Synchrotron based X-ray imaging techniques	**Jean Susini** ESRF, Grenoble, France
12:10-12:40	X-ray microdiffraction	**Christian Riekel** ESRF, Grenoble, France
13:00-14:00	***Lunch at the ESRF restaurant***	
Precipitation in Organic Environments		
14:00-14:30	Experimental studies on organic/calcite interactions: an overview	**Philippe Van Cappellen** Utrecht University, The Netherlands
14:30-15:00	Molecular dynamics simulations of calcite crystal growth processes	**Nora de Leeuw** University College London, London, UK
15:00-15:30	Studies on the inorganic/calcite sorption and co-precipitation: the Fe^{2+} and As^{3+} case	**Laurent Charlet** UJF, Grenoble, France
15:30-16:30	**Poster Clip (2 min per poster)**	

16:30-17:00	***Coffee Break - Poster session & Discussions***	
17:00-18:45	**Beamline Visit**	
19:30	***Bus departure***	
20:00-22:00	***Workshop Dinner***	
TUESDAY OCTOBER 31st		
Biomineralization		
08:30-09:10	Taking advantage of disorder: A widespread strategy in biomineralization	**Steve Weiner** Weizmann Institute of Science, Rehovot, Israel
09:10-09:40	A model of biomineralization in foraminifera and corals	**Jonathan Erez** The Hebrew University of Jerusalem, Israel
09:40-10:10	Cation incorporation into coccolithophorids	**Ros Rickaby** University of Oxford, Parks Road, UK
10:10-10:30	***Coffee break***	
10:30-12:00	**Discussions* / Poster session**	
12:00-13:30	***Lunch at the ESRF restaurant***	
13:30-14:00	The physiology behind coccolithophorids calcification	**Colin Brownlee** Marine Biological Association, Plymouth, UK
14:00-14:30	The common layered growth mode in coral and mollusk biocrystals	**Jean-Pierre Cuif** University Paris XI, Orsay, France
14:30-15:00	Hierarchical organization of calcite crystals in the red coral skeleton	**Alain Baronnet** CRMCN-CNRS, Marseille, France
15:00-15:30	Biologic polymers and confined water structure: the interplay hypothesis in bio-centered crystallization	**Lionel Mercury** Université Paris Sud, Orsay, France
15:30-16:00	***Coffee break***	
Session for Synthesis and Final Discussion		
16:00-17:00	Conclusive discussion	Moderator: **Steve Weiner** Weizmann Institute of Science, Rehovot, Israel
17:00-17:15	**Closure of the workshop:** Follow-up activities and ESF related business & opportunities	**Bernard Avril, Daniela Turk** European Science Foundation

2) Organisers report

In the wider context and with respect to the ESF networking programme, we were successful in bringing together members of four projects belonging to two EUROCORES Programmes in an attractive workshop. A total of 71 scientists from 10 countries involved with biologic/sedimentary calcification attended the WS:

71 scientists from 10 countries:

Austria	3
Belgium	3
Denmark	2
France	33
Germany	11
Israel	2
Spain	2
The Netherlands	4
United Kingdom	9
USA	2

The attendees saw the full scope of work in this field, from crystallography to organo-mineral interplay within biologically produced crystals. The workshop provided an opportunity to expose the diverse and sometimes conflicting view points and to develop integrated research plans from material applications to geological interpretations and from experimental to field data and modelling.

Within the EuroCLIMATE programme two main topics are addressed:

1. **Reconstructing past climates**
   - 1.1. Multi-proxy records from different archives
   - 1.2. Development of a common chronology for palaeo-records of marine, terrestrial and atmospheric processes
   - 1.3. Develop an understanding of existing proxies and develop new ones

2. **Modelling and understanding processes of past climates**
   - 2.1. The coupled climate system
   - 2.2. The carbon cycle
   - 2.3. The interactions between climate and vegetation

This WS specifically addressed the sub-topics under **"Reconstructing past climates"**. Climate reconstructions are generally based on the remains (biominerals) of once living organisms. Hence it is not surprising that the EuroCLIMATE participants were mainly from **PaleoSalt** and **Casiopeia** since these projects have a main interest in developing a mechanistic (process based) understanding of the incorporation of biogeochemical information (isotopes, elemental ratios) into hard parts of organisms ("proxy-bearers").

EuroMinScI focuses on the atomistic understanding of structures, properties and processes of minerals. The specific areas of research that were addressed in this workshop dealt with (bio)mineralization, structures and properties of amorphous materials and, trace elements and

isotope partitioning. It is therefore not surprising that members of **Cubcat** (dealing with prebiotic synthesis of biological molecules) and **BioCalc** (dealing with biomineralisation) were attracted to the meeting.

General Comments:

After the welcome address by William Stirling, the director general of the ESF, and the opening of the WS by Bernard Avril, the four project leaders shortly introduced their projects. The first topic organic and inorganic precipitations was introduced by 2 invited talks by Rich Reeder and Gernot Nehrke. This was particularly useful since it provided the baseline for element partitioning. This was followed by the introduction of synchrotron based methods: X-ray imaging by Jean Susini and X-ray microdiffraction by Christian Riekel. Most of us heard all of this for the first time and it was a real eye opener. The next topic was on precipitation in organic environments. Philippe van Cappellen, Nora de Leeuw and Laurent Charlet, discussed sorption and co-precipitation processes, organic/calcite interactions and, simulations of the molecular dynamics of crystal growth. This was followed by a short introduction of the posters, a poster session and a visit of several beamlines.

The next day was devoted to biomineralisation. Steve Weiner presented a state of the art introduction to the topic. This was followed by the presentation of a conceptual model of biomineralisation in foraminifera and corals (Jonathan Erez) and cation incorporation into coccolithophorids (Ros Rickaby). After lunch, the nannoscale level of biomineralisation (Jean-Pierre Cuif, Alain Baronnet), calcification physiology (Colin Brownlee) as well as a novel hypothesis for the role of water and its structure within a confined polymer space (Lionel Mercury) were discussed.

The WS was closed by a general discussion moderated by Steve Weiner and an outlook on further ESF activities and opportunities by Bernard Avril.

The overall feedback from the attendees was very positive: They appreciated the meeting with respect to both, the official program and the opportunities for discussions with members from other EuroCORE programmes. Visiting the ESRF beam lines was an exceptional opportunity for most of the participants, allowing them to directly discuss specific questions with physicists in charge of the analytical facilities.

The contact between the project members of **PaleoSalt** and **Casiopeia** has resulted in a closer exchange of ideas. In the future, we hope to conduct experiments in collaboration.

For EuroMinScI, two research projects can be considered as an immediate result of the Grenoble workshop
1 – G. Nehrke (EuroMinScI **BioCalc**) and C. Riekel (ESRF) plan a collaboration to better understand the crystallinity of calcite in planktonic and benthic Foraminifera in order to improve the crystallization models and the partitioning of both (trace) elements and isotopes.

2 – During the meeting free times a collaborationwas organized between Alain Baronnet and his team (Condensed Matter and Nanno Sciences laboratory, a CNRS unit in Marseille Luminy university) and members of the **BioCalc** group. This program includes:
- exploration of the structures ofthe nanograins in a a wider selection of biogenic calcites by using the to the method presented by Alain Baronnet for preparing ultrathin section for TEM observations

- Lionel Mercury (**BioCalc**), presented new ideas about the conditions of crystallization within the micrometer thick growth layer and the potential role of organics to induce critical changes in properties of water confined within the polymer network that is created by the biologic activity of the mineralizing organs.

Conclusion 1
The local organisation at ESRF was perfect! Jean Susini and Myriam Dhez were outstanding (thank you)! We can only recommend ESRF for future meetings of this kind.

Conclusion 2
This WS has provided initial contacts between 4 projects within 2 EuroCORE programmes. We recommend that future funding from ESF should be made available to strengthen these initial contacts.