# BioCalc project in EuroMinSci

Eurocores Programs



Field and Lab. controlled growth of calcareous proxy-bearers

Fluorochrome time-marking

Environment recording

The

Chemical and Isotopic Fractionation Modelling

Mineral-Organic **Template effect** 

at the Mineral-Organic

Minor element uptakes in crystal lattices

Microstructural characterizations

> **XANES** biochemical mapping

> > Biochemical characterization of organic matrices

**BioCalc** Force Fields project Interface

> Chemical Localized Chemical and Isotopic mapping Measurements

 $\delta$  ref.

## The BioCalc background

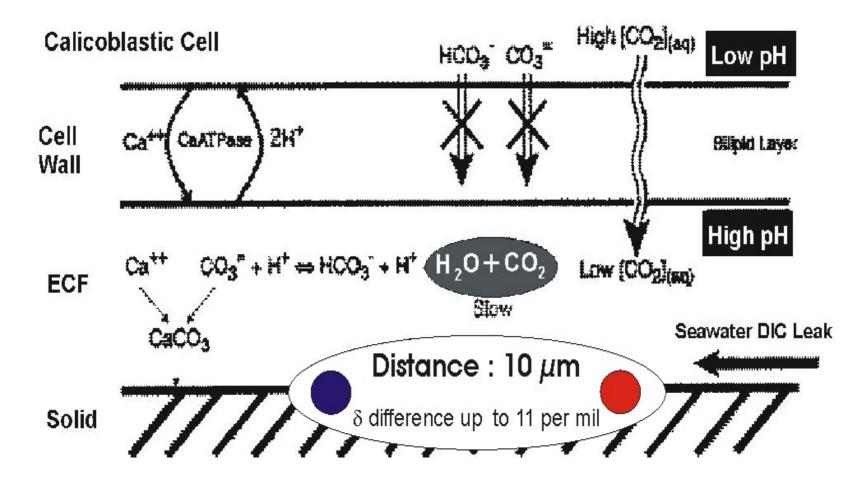
- Biologically produced Ca-carbonates are among the most important sources of information used in climate change studies but, surprisingly, no agreement exists about the crystallization mechanism that produces these widely used biological archives. More precisely, a fundamental contrast is observed between the geochemical and biological approaches
- In the geological area, interpretations of chemical or isotopic signals (the "proxies") are based on the concept of a crystallization governed by purely chemical mechanisms

- Crystallization is believed to occur within an homogenous volume of fluid, the properties of which being "close to sea water" (McConnaughey 1989).
- Biological activity is limited to "enzymatic ion transport" of Ca2+, creating the required conditions of supersaturation for CaCO3 precipitation. The skeleton material is interpreted as a purely mineral mineral product and no attention is given to the sizes, shapes and three-dimensional arrangements of the resulting crystals.
- Barnes (1970) for instance, simply suggested that "crystal growth competition" could be the mechanism leading to spatial arrangements of crystals

- Urey et al. (1951) had suggested the possible influence of a "vital effect". Rapidly, undisputable examples of taxonomy-linked responses to environmental changes were established (i.e. the synthesis of the results on corals from Pacific ocean by Weber and Woodhead, 1972).
- Evidence that distinct species sharing the same water pool record differently the variations of the environmental parameters led to necessity of a "calibration" before using any organism as environmental archive.
- This results in a multitude of species specific equations and, actually, leads to a basically empirical approach of the biological records.

- Additional and still more intriguing feature of environment recording by biogenic Ca-carbonates has occurred during the last decade.
- High resolution measurement devices have made obvious that important differences in isotopic fractionations do exist not only between skeletons built by distinct species but within different regions of the skeleton of a given specimen.

### Adkins diagram



# Biomineralization patterns and Microstructural analysis in Coral skeletons

- Progress that have been made during the two last decades in understanding the way by which organisms control the formation of their mineralized structures allow to develop a new approach in microstructural analysis of calcareous inveterbrate skeletons.
- The reason is that in any "matrix-mediated" calcareous hard-parts, the permanent interplay between the specifically secreted organic compounds and mineral ions can be easily evidenced at the micron-scaled observation level.

- Mineralizing matrices that are cyclically secreted remain associated to the mineral component of which they have controlled the development during each of the growth steps.
- The major consequence is that, in spite of a crystalline appearence, crystal-like units that build any biologic calcareous skeletons are actually organo-mineral architectures.
- The micron-scaled growth steps can be distinctly retrieved by preparative processes acting on the differential solubility between organic rich and organic depleted zones.

- Detailed growth history of skeletal units can be etablished, allowing to replace the purely geometrical descriptions of calcareous skeletal components by a time-based study of their development.
- Important changes in both basic microstructural concepts and meaning of traditional descriptive terms (prisms, lamellae, fibres etc..). In addition, this approach leads to various and important practical consequences.

- Under these two respects, Scleractinian corals are of particular interest:
- Since the beginning of corallian studies, taxonomy and evolutionary interpretations are mostly based on detailed descriptions of hard parts.
- A steady increasing use of coral skeletons as environmental archives by use of chemical or isotopic measurements, both requiring the most accurate checking of the diagenetic status of used specimens.

- Description of coral skeletons by a biomineralization—based microstructural analysis.
- New view about the "two-step growth process" of coral skeletons

- Physical evidences support the hypothesis of a specific secretory process at the extreme tip of the growing elements, generally leading to crystallisation of microcrystalline material.
- In parallel with differences that can be observed in fine structures of skeletal fibres, early crystallization mechanism in centres can also produce variously crystallised material from species to species, probably depending upon the biochemical compositions of mineralizing matrices.

- Presence of organic material associated to calcified structures has long been recognized, but understanding of their biochemical composition has substantial progress in the second half of last century.
- Since the pioneering observations by Goreau (1959), investigators have emphasized the very specific properties of these biochemical compounds always associated to calcareous biominerals.

- Very high molecular weights and low isoelectric points are now proved to be common patterns for these complex hydrated-glycoproteins.
- Such particular properties have led investigators to suggest an active role in the crystallyzation process for these specifically secreted organic assemblages

- In some mineralized tissues, a layered organization is well visible: the nacreous part of some mollusc shells is the most famous exemple. Grégoire (1961), has shown the close association of organic components with these mineral units and the remarkable persistency of these organics sheets in fossil materials.
- Through specific preparative process, it has been shown that all the elongated crystal-like skeletal units (as the *Pinna* prisms below, the coral fibres etc..) also result from superimposition of elemental growth layers of a few microns in thickness.