Ca-carbonate biomineralizations

Historical background

History of biomineralization research

- Ca-carbonate mineralizations are produced by a large range of organisms. These biominerals, exhibit properties (shape, composition...) that are never found in the non biogenic calcite or aragonite.
- Their two major specificities have been recognized since the middle of the 19th century.
- All these material have in common :- a taxonomy-linked three dimensional arangement of crystal units and a permanent association with organic materials.

History

Progresses in understanding the relationships between the two components have been extremely slow and only in the last decade, technological improvements allow to access to the molecular level at which the permanent interplay between organics and mineral component can be investigated.

History

- As soon as 1844, Bowerkank was able to describe the topographical arrangements of some layers in mollusk shells. Then a major paper was due to Boggild (1930) who described the main microstructural types and their arrangements in the mollusk shells, and show that they are taxonomically dependant.
- Then, topographical relationships between thick organic membranes and mineral units were observed on some propitious structures (nacreous layer of mollusks, large calcitic prisms) with optical, then transmission electron microscopes (TEM) (Grégoire et al. 1958-1980 ; Wada 1956-1985).

History

- The layered ultrastructures of these membranes were described for the nacreous layer (Wada, Nakahara 1960-1990), mainly in gastropod shells. But it appears that within the mineral units, organic matrices are also present. These components were not seen with the used techniques, because the samples have to be demineralized.
- Scanning electron microscopes (SEM) allow to study the samples without demineralization. Despite the lower magnification and resolution, it has been possible to show that the mineral units (nacreous tablets, calcitic prisms), were not actual units. They were composed of subunits (Mutvei 1964-1991), taxonomically dependant.

Analytical techniques

- **Analysis of the microstructures and nanostructures of the skeletons of selected carbonate biominerals : corals, mollusks and eggshells.**
- **Then, the organic matrices will be extracted from within the skeletons, and biochemically characterized.**
- **The extracted organic matrices will be fractionated (according to their molecular weights, and/or isoelectric points), and specific antibodies will be produced.**

Scanning Electron Microscopy

- It has long been observed that skeletons of scleractinian corals are built by precisely arranged fibres (E. Pratz, 1882). SEM observations show that fibres are linear elements (1) and polarized light observation of thin sections demonstrates their crystalline behaviour (2).

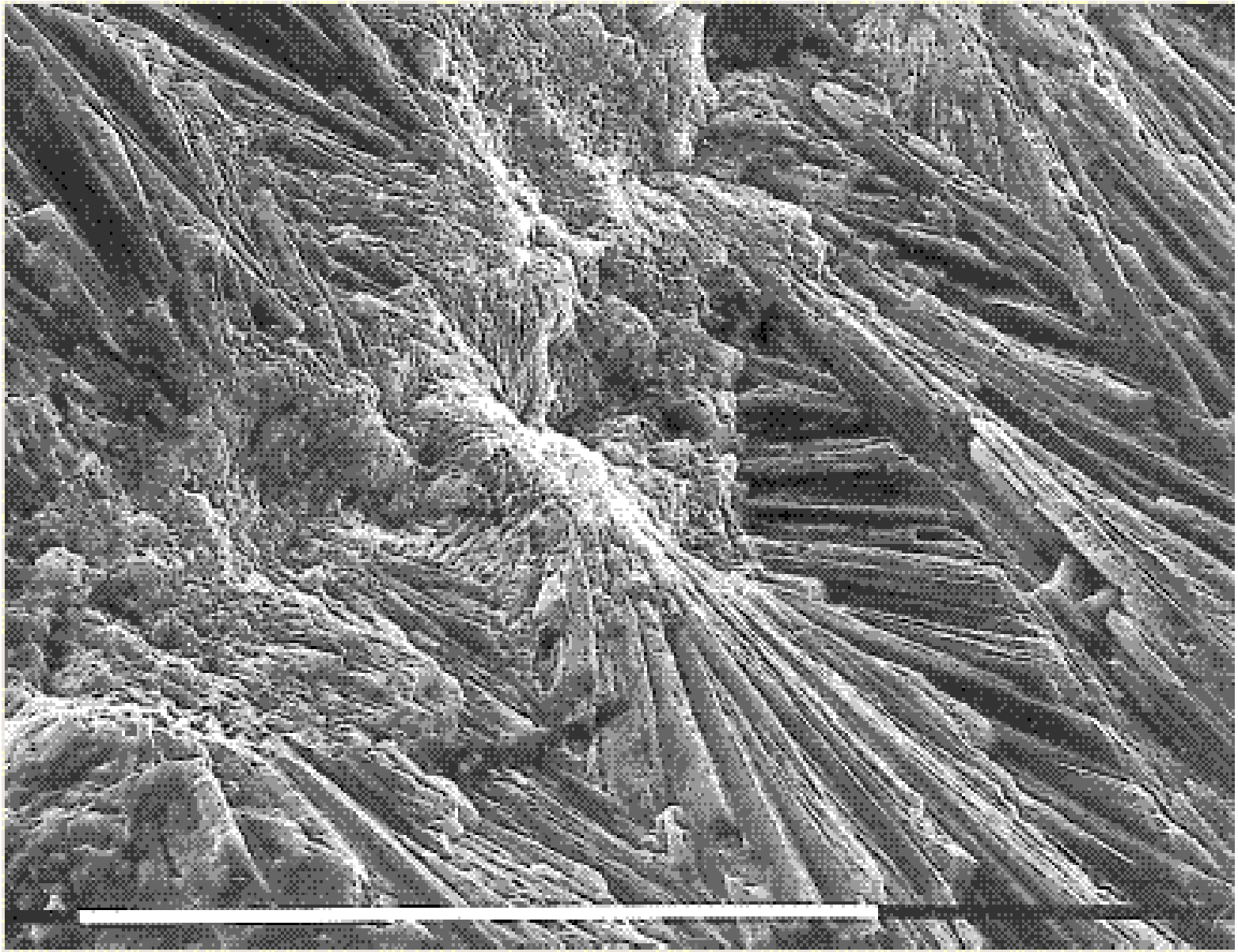

Figure 1 Groups of skeletal fibres in coral septum.

Bar 100microns

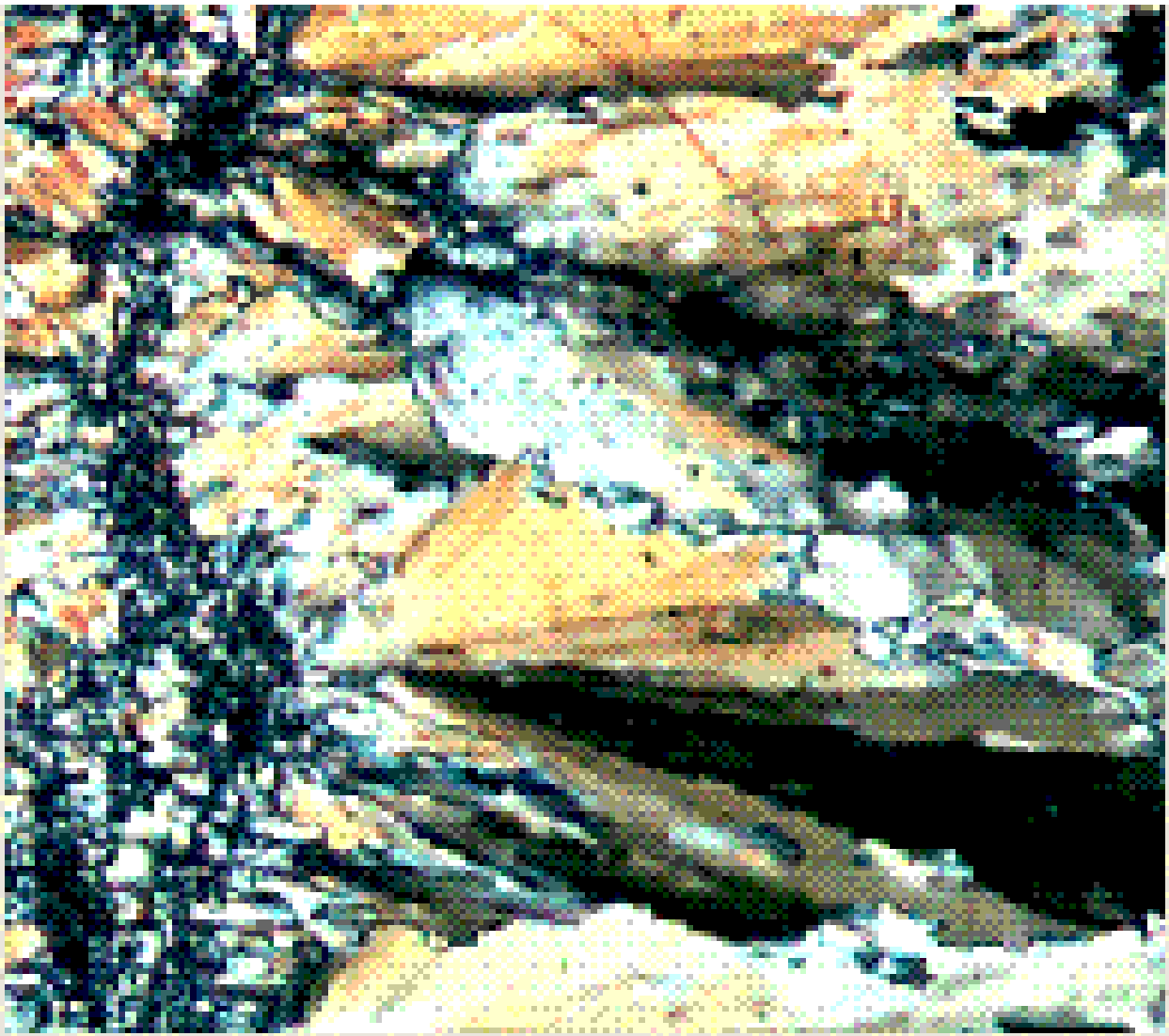

Figure 2 : Thin section of similar sector observed in polarized light

- In parallel, etching processes applied to polished surfaces prepared in coral skeletons provide us with pictures that demonstrate the heterogeneous nature offibres.
- Differential solubility in fibres reveals the presence of coordinated growth lines(3 and 4), allowing to visualize the successive positions of the basal ectoderm that remain marked within crystal-like fibers themselves.

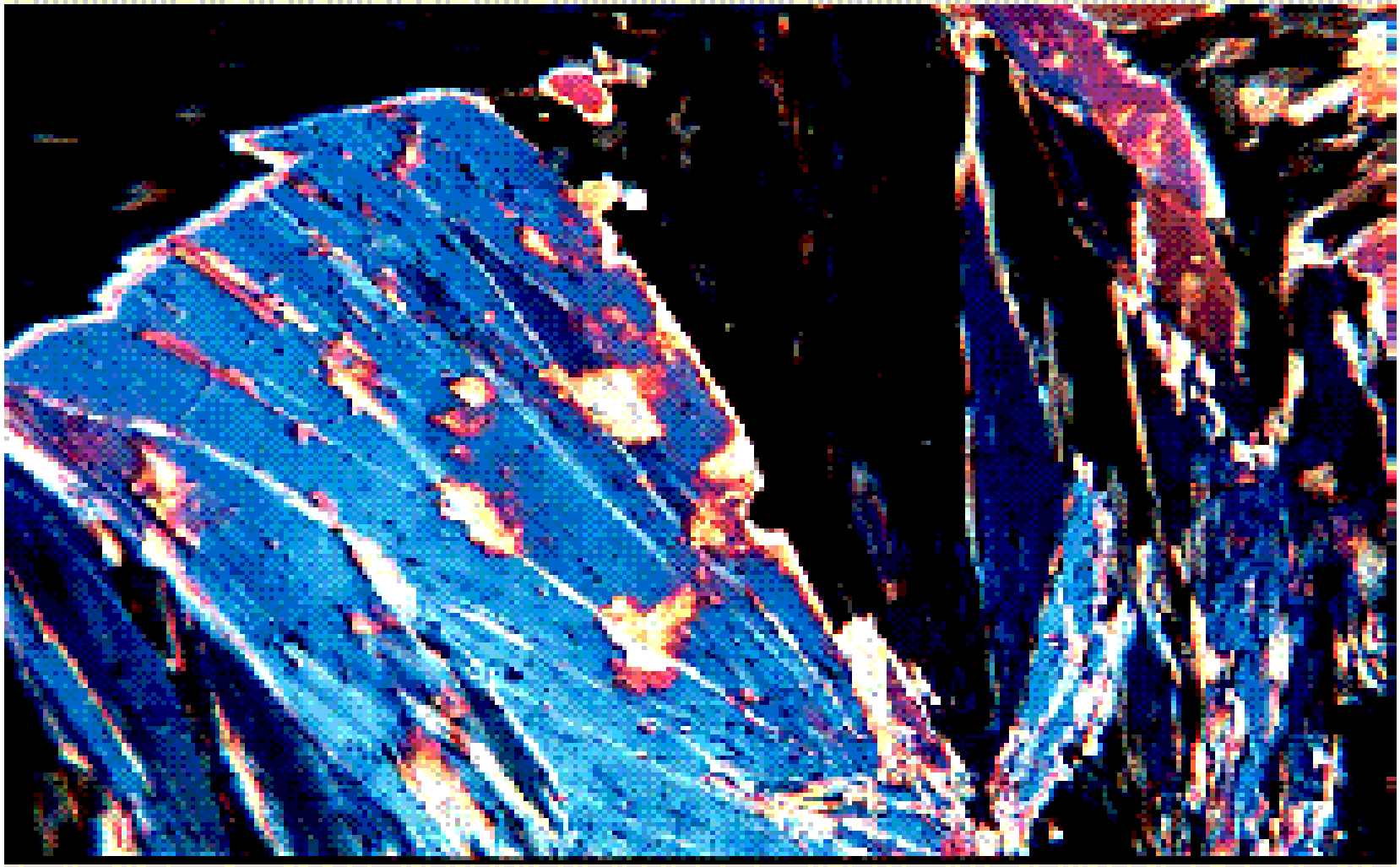

Figure 3 : Thins section of groups of fibers; purely crystalline behaviour in polarized light

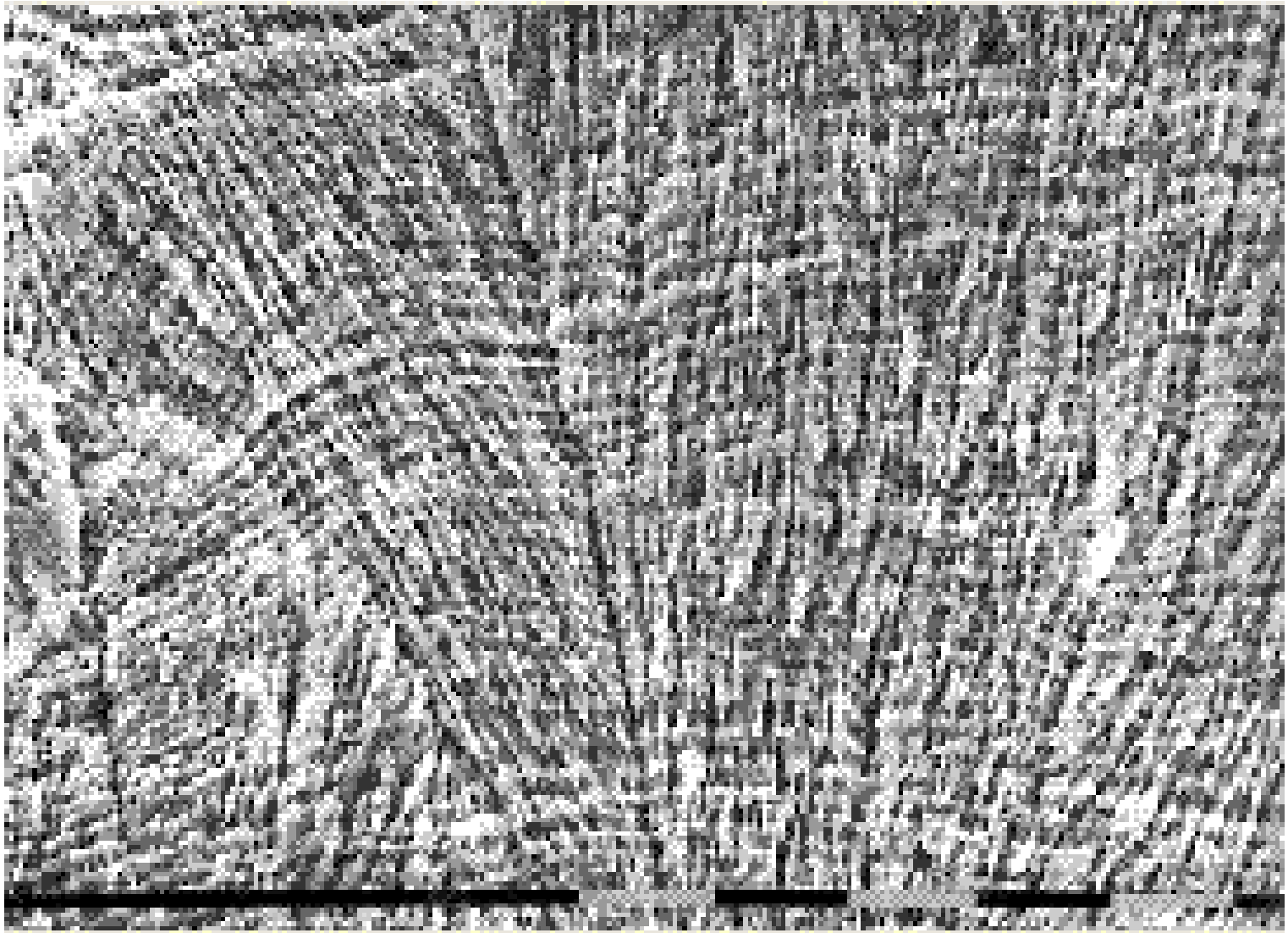

Figure 4 SEM view of the same sector after etching process. Differential solubility of growth zonation is well visible

- Interpretation is that differential solubility is caused by variation of the organic/mineral ratio that occurs during each biomineralization cycle, although no integrative model is presently available to precisely explain the operating mechanism of this organo-mineral association, from the molecular scale to the observable micronic level.

- Coral fibers cannot be longer considered as purely crystalline units. They are composite (organo-mineral) structures, and their organic component can be analyzed with two respects:
- Its repartition within skeletal elements, that provide us with precise information concerning morphologic changes that have occurred during coral growth: see below, new pictures of the two-step corallian growth process.

Economic Interests

- Two main domains provide us with interesting topics linked to industrial activity or medical sectors.
- Monitoring aquacultural sites through analyses of disturbance in shell mineralization appears to be an an easy and efficient way to control growth conditions of molluscs of economic interest (i.e. *Oyster*, *Pecten* etc.). In the pearl industry, this approach is also useful to check the quality of mineralization layers in pearls, and to study spreading and suppression of various calcification troubles that occur sometimes in over-exploited lagoons.

Economic Interests

- In agriculture, the egg shell is of major importance as a microbian barrier and its thickness play a role in the resistance to breakage.
- Use of coral skeleton modules as graft-material in bone repair surgery is a rapidly evolving technique. High resolution study of microstructural patterns and biochemical characterization of taxonomically linked mineralizing matrices help us in selecting the most suitable species to be used in the bone repair process.