ABSTRACT. — The negative effects of quartz on biological systems are well known, from a clinical point of view, since the XVIII century, anyway the influence of quartz on the marine benthic organisms and communities is underestimated. Interactions between organisms and minerals (biomineralogy) could play a major role on the life cycle of a species and on the spatial distribution and structure of marine and freshwater benthic communities. Various biosystems, at different levels of complexity (cell, organism, species, and community) show, in fact, the ability to recognise, select, react, and possibly use the mineral fraction. A negative influence of quartz on the biological activity has been demonstrated, due to the toxic activity of the silanolic radicals on the surface of the crystalline quartz, which interferes with animal metabolism.

The aim of this paper is to review the selective response by benthic organisms to the quartz presence and evaluate the primary role of quartz in affecting the development, settlement and growth of many species. Such selectivity may cause spatial anomalies in species composition, diversity and biomass in marine and freshwater communities and, consequently, have important consequences on basic and applied ecology.

KEY WORDS: sponge, substrates, diatoms ecology, sedimentation.
INTRODUCTION

In the last decades great attention has been paid to the process of deposition and dissolution of biominerals, mainly carbonates, that have a particular role in the marine community dynamics (McCall and Tevesz, 1982) and a fundamental importance in the CO$_2$ budget.

On the contrary less attention has been paid to the biomineralogy that is the complex of interactions between biological systems, at different levels of complexity (cell, organism, species, and community), and the mineral substance they come in contact within the marine and freshwater environments. Various biosystems, in fact, show the ability to recognize, select, react, and possibly use the environmental mineral fraction. The reactions towards different minerals may be very different: it is well known, for example, that crystalline silica (quartz) acts differently from amorphous opal and chalcedony. In several vertebrates, for example, the inhalation of quartz dusts is responsible of severe lung diseases like silicosis and bronchogenic cancer (Donaldson and Borm, 1998).

The aim of this paper is to review the primary role of quartz in affecting the development, settlement and growth of many aquatic species. Such selectivity may cause spatial anomalies in species composition, diversity and biomass in marine and freshwater communities (Cerrano et al., 1999a; Bavestrello et al., 2000; Guidetti et al., submitted) and, consequently, have important influences on basic and applied ecology.

PATHOLOGICAL EFFECTS OF QUARTZ

While quartz (crystalline silica) seems to have a negative effect at different biological levels, no diseases related to the amorphous form have ever been reported (Iler, 1979). Toxicity of other forms of silica, such as diatomaceous earth, is still much debated (Fubini et al., 1989; IARC, 1997).

Although the pathogenic potential of quartz as rock–forming mineral is already well known, the action at cellular level is still substantially unclear. This activity could be related to chemical processes taking place at the surface of grains in contact with the cells (Fubini and Wallace, 1999). Several factors have been identified to contribute to the onset of a chronic inflammation process in vertebrates, among which, ROS (reactive oxygen species) production. Lipid peroxidation is activated during this process, with subsequent interference with arachidonic acid metabolism and damage to DNA (Fubini, 1998), followed by the release of cytokines (Lardot et al., 1998), and nitrogen oxide (Blackford et al., 1997).

The study of these processes requires a detailed knowledge of the hydrophilic and/or hydrophobic properties of the different silica forms (Bolis et al., 1991), while biochemical studies will be necessary to evidence the role of ascorbic acid in increasing toxicity of some silica polymorphic forms towards cell lines (epithelia and macrophages). The outcome of this research is expected to shed new light on toxicity mechanisms of quartz powders, not only in animal models, but also in the case of human silicosis.

Finally, chemical research should interpret and justify, from a surface structure point of view, molecule interaction and behaviour patterns when the cell comes in contact with the mineral to be recognised.

COMMUNITIES LEVEL

Regarding soft bottoms communities in situ experiments on the development of meiofauna, evidenced that, in artificially enriched sands containing different percentages of quartz, the biomass and the specific structure of the meiobenthic community are inversely proportional to the amount of present quartz, suggesting a significant inhibition due to the quartz presence (Cerrano et al., 1999a).

The effects of the mineralogical composition
of rocks as dolostones, limestones, serpentinites, basalts, gabbros, quartz–arenites, granites, quartzites, on the marine hard bottom communities' structure, in comparable conditions of food availability and water movement, have been studied in different Mediterranean areas (Liguria, Tuscany Archipelago, Sardinia) (Bavestrello et al., 2000; Cattaneo–Vietti et al., 2002; Faimali et al., submitted).

To discriminate substrate–related–variability from space–variability (as samples closer in space should be more similar to each other than those further apart), it was necessary to use an appropriate spatially multi–resolution nested sampling design (Underwood and Chapman, 1996). Concurrently, to avoid small–scale patchiness of substrate, observations were performed at two different spatial scales (400 cm² and 10,000 cm²).

Results demonstrate that benthic communities growing on quartz–rich rocks (quartz–arenites, granites, quartzites) are less diverse and show a simpler physiognomy compared to those growing on carbonatic rocks (Bavestrello et al., 2000; Faimali et al., submitted) (Fig. 1). However, each taxa may respond in different way: vermetids, for example, are significantly more frequent on granitic substrates in comparison with carbonatic ones. This group of sessile, filter feeders gastropods are in fact favored by algal–free substrata as occurs on the Sardinian granite rocks, since algal canopy disturb their trophic activity (Schiaparelli and Cattaneo–Vietti, 1999).

The overall negative quartz effect acts mainly during the early stages of colonization and gets reduced as the succession goes on. Many sessile organisms, in fact, lay calcareous structures that offer a secondary substrate to later colonists, thus annulling the quartz effect. This could be the case of encrusting macroalgae and bryozoans which operate a «biological conditioning» of the substrate.

Nevertheless, the quartz effect could be maintained in high energy communities or where the grazing is heavy, because these frequent disturbs produce periodical population «zeroing», which prevents the community to reach a mature condition and exposing bare quartz–rich substrates.

PIONEER COMMUNITIES

The structure of macrobenthic communities is often influenced by microbial films (Scheltema, 1976). The settlement of the marine bacterium *Vibrio coli* on sand grains of different mineralogical composition clearly evidences that calcareous substrata are more suitable for bacterial adhesion than quartzitic ones.

Studies of early development of marine benthic communities on quartz and amorphous silica (opal) evidence an important role played by minerals in structuring the biofilm. The growth of diatoms, one of the main components of the biofilm, is influenced by the availability of different silica sources. Three diatom strains: *Cylindrotheca fusiformis*, *Navicula* sp., *Skeletonema costatum* incubated in controlled conditions, with mineral (quartz sand and two pure quartz dusts with variable degree of hydrophilicity/hydrophobicity) and biogenic (diatomaceous earth and sponge spicules) silica substrates showed different growth patterns. Higher values of growth were showed with quartz particles while, in contrast, low values of growth were found in the presence of the biogenic amorphous silica substrates. The high value of the silicon uptake of all diatom species in the presence of the crystalline substrates in culture conditions seemed to confirm the preferred exploitation of silicon from crystalline sources with respect to the amorphous biogenic mineral substrates. Thus, the uptake is not mediated by solubilised oligomeric silica but by a direct interaction between diatoms and the solid substrate. Such interaction is highly specific either for diatom species and silica particles (Penna et al., 2003).
Fig. 1 – Mean (±1 standard deviation) number of species (a) and total substratum cover (b) of the epibenthic assemblages in three sites characterised by different mineralogy. For each site, quartz–rich rocks (quartzite or granites) (white bars), and rocks poor in or deprived of quartz (grey bar) are represented (from Bavestrello et al., 2000).
AUTOECOLOGICAL ASPECTS

Many benthic species react differently in presence of some kinds of silica, suggesting the existence of complex mechanisms to recognize and select, at cellular level, the different surface properties of the mineral.

Sponges, which have a modest or absent spicular component in the skeleton, often incorporate foreign materials such as opaline spicules, quartz and silicate grains dropped on their surface. Generally, this matter is incorporated into the collagenous fibers for strengthening the sponge skeleton (Teragawa, 1986a, b). This is one of the most interesting and yet least known behaviour in sponges (Bavestrello et al., 2003).

The common Atlanto–Mediterranean demosponge Chondrosia reniformis (Bavestrello et al., 1995; 1996; 1998a, b), in a high sedimentation environment, is forced to select the settled material, thus avoiding to incorporate high amounts of carbonates, which are the most abundant settling fraction, as confirmed by the comparison on trapped material collected near the investigated sponges (Bavestrello et al., 1996). In fact, the percent composition of mineral grains found in the sponge (quartz, plagioclase, sanidine, muscovite, chlorite, sodic amphibole and opaline spicules) mirrors always the trapped sediments, except for the lack of carbonates (calcite and dolomite) which are predominant in the sediment.

This selectivity can be switched on and off during the species biological cycle. During asexual reproduction, in fact, propagules of this species acquire a sort of affinity also for carbonates, thus allowing the sponge to settle also on this type of substrate (Bavestrello et al., 1998b).

The quartz selection is performed on the sponge surface (pinacoderm), which also differently reacts to different forms of silica. When the quartz grains settle on the sponge, the pinacoderm breaks and the pinacocytes contract themselves to form a rim around them.

Photo 1 – A : Foreign bodies gradually engulfed by the cells of the sponge surface (pinacocytes) in Chondrosia reniformis. B: Quartz grains in different phases of engulfing (a) and spicule completely enveloped by pinacocytes. (Scale bars. a: 50 µm; b: 5 µm) (from Bavestrello et al., 2003).
(Photo 1a), while the presence of opaline spicules elicits a motile response of pinacocytes that quickly recover them (Photo 1b).

In the sponge body these two kinds of silica have different fates: the quartz grains are strongly etched (Photo 2), rounded, made uniform in size (about 30 µm) and expelled as pellets, while the amorphous silica (chalcedony and opal) are stored (Bavestrello et al., 1995).

The SiO₂ dissolution is evidenced, in laboratory, by a sharp increase of dissolved silica in the water where quartz–treated sponges were reared: over 50 hours the dissolved silica reached a maximum value of 0.1 mg/l, starting from zero.

The dissolution process of quartz in Chondrosia reniformis is due to the ascorbic acid activity, which reaches in sponges levels from 1 to 10 µg/g wet weight of tissue. Such acid represents the reducing agent of the proline hydroxilation in collagene biosynthesis in the sponge (Garrone, 1978) and, owing to its antioxidant properties, is likely to act as an inhibitor in the competition for substrate or as an antifeeder (Cerrano et al., 1999b). The quartz dissolution mechanism by ascorbic acid has been partially clarified: it is supposed to change the quartz surface features, leading to an increased radical production (Fenoglio et al., 2000).

A possible relationship between silica turnover and symbiosis may be postulated. The Mediterranean sponge, Chondrilla nucula, presenting a remarkable population of autotrophic symbionts, increases its biomass during summer months and its spicules show impressive signs of corrosion (Bavestrello et al., 1993). This phenomenon suggests a drastic increase of the ascorbic acid levels to protect against the increasing levels of free radicals due to the increased photosynthetic activity. It is possible to speculate that in such conditions, the levels of ascorbic acid in the sponge tissues become so high to determine the partial dissolution of the sponge spicules.

**Larval ecology**

The adhesion of the dispersion phases (larvae, asexual propagula) of sessile organisms to a substrate is a key event in the biological cycle of the species and the mineral nature of the substrate plays an important role in this process. In many invertebrates, the adhesion culminates with the larval metamorphosis, which can be fully performed in all its complex phases only after the larva has successfully settled on a properly selected substrate, thus avoiding any negative impact from an unsuitable substrate to its growth. Considering that free–swimming larvae have generally limited chance of survival (some days at maximum), their ability to interact with the substrate is fundamental.

In laboratory experiments it was observed that the cypris settlement of the barnacle Balanus amphitrite is influenced by the nature
of substratum (Faimali et al., submitted) as well as by biofilms structure. In addition, the biofilm formation is influenced by the substratum (marble, quartz, glass, and cembonit), as number of settled micro–organisms and microbenthic community biodiversity, which could depend not only on chemical nature of the substrate, but also on its microtexture. With biofilm ageing, the attractiveness of different substrates tends to disappear.

Laboratory studies on the larval ecology of hydroids have showed that the crawling planulae of Eudendrium glomeratum have a five fold stronger selectivity for carbonates than quartzitic sediments (Bavestrello et al., 2000).

Also among the sessile marine tunicates, the selection of a suitable substrate by the larvae is an important and critical factor determining the distribution of species. Laboratory experiments showed that larvae can discriminate between the substrates based on their silica content. Surprisingly, surface roughness did not influence larval attachment. Under the same laboratory conditions, the larvae that attached to quartzite grew faster and had a wider area of contact with the substrate than those that grew on carbonaceous stones (Groppelli et al., 2003).

Clear evidence of quartz action was observed also in the development of a freshwater fish, the cichlid Pelvicachromis pulcher. Laboratory tests have shown that this species selectively chooses the type of substrate where to lay eggs (Maradonna et al., 2003). Quartz, in fact, interferes with its development: while 90% of embryos placed in a carbonaceous sand have successfully metamorphosed, 100% of embryos placed on quartz–rich sand died on day 8 of their development.

In the larvae grown on quartzitic substrate, a decreased expression of most of the genes analysed was observed. In fact, IGF–II, one of the most important fetal growth factors, was found to have less expression in the larvae developed on quartz. Looking at the GADPH, we found the expression of this gene to be totally inhibited in the larvae developed on quartz. GADPH is one of the key enzymes of the glycolytic pathway through which the cells produce ATP.

In the same larvae, only the molecular chaperone HSP70, which is involved in the folding of the nascent polypeptide chain (Kelley, 1999), was found to have a higher expression. Since it has been reported that induction of HSP70 makes cells more resistant to a number of cellular injuries (Mayer et al., 2000; Airaksinen et al., 1998; Misra et al., 1989; Mosser and Bols, 1988), the higher levels of this gene found in the present work indicate that the quartz represents a source of stress for the larvae, which attempt to recover through an over–expression of HSP70.

CONCLUSIONS

Several abiotic factors (water temperature, moisture, light and water movement) are considered involved in the spatial distribution of benthic marine organisms. The results of the studies conducted on the interactions between biological aquatic systems and silica indicate that the well known pathogenic effects of quartz on mammalian lungs represent only an example of a more wide phenomenon involving, at different levels (larval ecology, development and species life cycle), all the invertebrate groups. This response to the presence of quartz, which is so widespread in nature, could explain possible differences and anomalies found in the structure of marine communities, due to quartz toxic action.

The unsuspected ability to recognize, select and use amorphous silica and quartz rocks, by different groups of protists and lower metazoans indicate the importance of the surface properties of minerals in the interactions with cells.

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REFERENCES


evaluation of carcinogenic risk to humans. Vol. 68, Lyon, France.