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Minerogenetic activity of the marine sponge *Chondrosia reniformis* and local impact on sediment composition

Gabriella Lucchetti[1]*, Laura Gaggero[1], Giorgio Bavestrello[2],
Carlo Cerrano[1] and Riccardo Cattaneo-Viétti[1]

[1] Dip. Te. Ris. - Dipartimento per lo Studio del Territorio e delle sue Risorse. Università di Genova,
Corso Europa 26, I-16132 Genova, Italy
[2] Istituto di Scienze del Mare. Università di Ancona, Via Brecce Bianche, I-60131 Ancona, Italy

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Abstract. — The capacity of the demosponge *Chondrosia reniformis* to selectively incorporate and elaborate inorganic materials is described. The sponge actively engulfs sandy grains of various silica-bearing minerals, such as quartz, opale, chalcedony, feldspars, mica, chlorite, amphiboles, etc. Conversely, carbonates are rejected, at different stages during the sponge biological cycle. Different ectosome activity towards quartz and opale is evidenced by the sponge capacity to differentially react to different crystallographic forms of silica: while opale and chalcedony are stored in the collagenous fibres, quartz is dissolved and residual rounded micrograins (3-5 μm) are ejected. The ascorbic acid produced by the sponge is considered to be the agent for quartz dissolution. Finally, the production of calcium oxalates (whewellite and weddellite) and gypsum by the sponge, and their release in the surrounding sediment is evidenced.

Riassunto. — La spugna *Chondrosia reniformis* possiede la capacità di incorporare in maniera selettiva materiali inorganici appartenenti a diverse specie mineralogiche. Quarzo, opale, calcedonio, feldspati, mica, clorite, anfiboli, etc. vengono inglobati; al contrario, i carbonati sono espulsi tranne che in alcune fasi del ciclo biologico. Inoltre la spugna è in grado di reagire selettivamente nei confronti delle diverse forme della silice: mentre opale e calcedonio sono incorporati nell'ectosoma, il quarzo inglobato viene portato in soluzione, probabilmente per azione dell'acido ascorbico prodotto dalla spugna, ed i micrograuli (3-5 μm) residui vengono espulsi. Infine, la spugna produce ossalati di calcio (whewellite e weddellite) e gesso che sono osservati sulla superficie dell'ectosoma e vengono rilasciati al sedimento circostante.

Key Words: *Biomineralogy, quartz dissolution, calcium oxalates, gypsum.*

Introduction

Many demosponges (Porifera) are able to select and engulf inorganic detrital materials such as opaline spicules, quartz and silicates, dropped on their ectosome (the sponge epithelium). Generally, this matter is incorporated into the collagenous fibres in order to strengthen the sponge skeleton (Teregawa, 1986; Pronzato *et al.*, 1998).

The common Atlanto-Mediterranean

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* Corresponding author, E-mail: lucchett@dipteris.unige.it

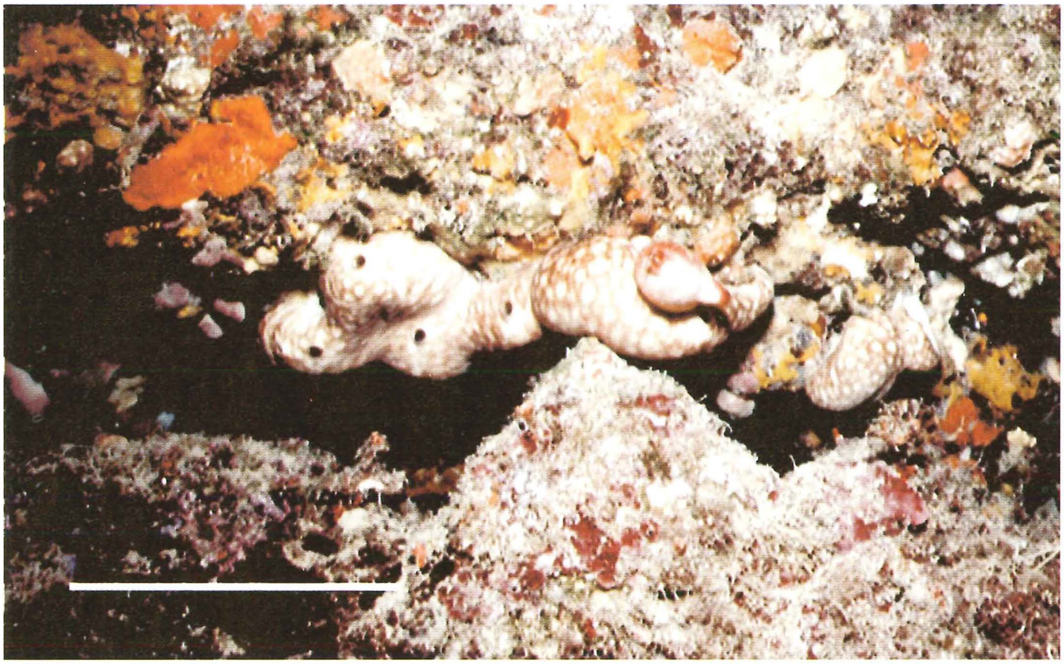

Fig. 1 – *Chondrosia reniformis* living along the Portofino cliff. Bar scale = 10 cm.

demosponge *Chondrosia reniformis* (fig. 1) engulfs large amounts of minerals to enforce its body, for it has no spicular skeleton. This sponge is capable of incorporating inorganic (allochtonous) materials (up to 3000 grains/cm^2), selectively engulfing the mineral phases, and actively processing them.

In particular, the sponge ectosome is able to:

– select carbonates from quartz and other silica-bearing minerals (Bavestrello *et al.*, 1996),

– attack and selectively dissolve the engulfed quartz, while chalcedony and opale are incorporated and stored (Bavestrello *et al.*, 1995a),

– biosynthesise calcium minerals, like oxalates (Cerrano *et al.*, 1999) and gypsum.

As a consequence of this activity, the mineral composition of neighbouring sediments is often significantly affected.

This paper presents recent literature and new data on these biologically-induced minerogenetic processes and elaborates on them from an earth-sciences perspective.

LOCALIZATION OF SAMPLES AND ANALYTICAL METHODOLOGIES

In order to investigate the interaction between minerals and *C. reniformis,* 10 specimens were collected along the Portofino cliff (Ligurian Sea). This cliff developed in conglomerates of Oligocene age mainly consisting of marly limestone and subordinate ophiolitic or granitic clasts in arenaceous-carbonatic matrix. In order to evaluate the contribution of the sponge minerogenetic activity to local sedimentation, three sediment traps were placed within Portofino's *C. reniformis* population, on a vertical cliff, at 10, 15, and 25 m depth.

For comparison, many specimens of *C. reniformis* and sediments have been collected from different Mediterranean sites (Gallinara Island and Nervi, Zoagli, Laigueglia cliffs in the Ligurian Sea; Corsica, Elba, Ustica Islands, Palinuro and Vaticano Capes in the Thyrrenian Sea; Tremiti Islands in the Adriatic Sea and Cyclades Islands in the Aegeus Sea).

The external surfaces of sampled *C. reniformis* were observed by SEM (Philips 515); the sponge ectosome was then dissolved in NaClO 5% and the inner mineral fraction was determined using XRD and an EDS-equipped SEM.

The presence of dissolved silica in the water was checked after 0, 13, 24, 37, and 48 h (molybdosilicate method, Bavestrello *et al.*, 1995a); on *C. reniformis* samples, HPLC analysis (Lloyd *et al.*, 1987; Rose and Bode, 1995) of ascorbic acid was carried out.

SPONGE ECTOSOME SELECTIVITY IN MINERAL UPTAKING

No evidence of grain size difference was found by comparing the inorganic matter uptaken by *Chondrosia reniformis*, living along the Portofino promontory cliffs between 10 and 30 m depth, and the inorganic detritus from sediment traps placed close by. This would thus suggest that no selection of this sort is made by the sponge. However, important differences were observed in mineral composition: calcite in the form of crystalline grains or biogenic fragments is the main constituent, with minor quartz, albite, chlorite and opaline spicules, of the same matter collected in the sediment traps. Conversely, it is very rare among engulfed phases. Moreover, while gypsum and oxalates occur in sediments collected by traps adjacent to the sponges as well as within the sponge ectosome, they are not to be found in sediments collected far from the sponges.

The ability of the sponge to avoid calcareous matter is confirmed also for *Chondrosia* collected from different Mediterranean sites (Bavestrello *et al.*, 1995b). In such areas, calcite, Mg-calcite, and more rarely dolomite, are present in variable amounts, together with quartz, plagioclase, sanidine, muscovite, chlorite, sodic amphibole, and opaline spicules. Everywhere, the modal percentage of mineral grains in the sponge reflects their modal content in the trapped sediments, except for the virtual absence of carbonates. Also, surface morphology (crystal faces, cleavages of sharp-edged fractures) and the size range of incorporated opaline spicules and silicates corresponds, except for quartz (fig. 2*a*), to those of the grains in the trapped sediments. Conversely, quartz grains within the ectosome are rounded with spongy surfaces (fig. 2*a* and *b*), due to the development of a microalveolar structure.

Selectivity towards carbonates occurs only when the sponge is fixed to the substratum. During its asexual reproduction, the lower ectosome of its free propagules (fragments of the sponge tissue devoted to asexual reproduction) can adhere to both calcareous and siliceous substrata, giving them the opportunity to settle also on calcareous substratum (Bavestrello *et al.*, 1998).

UPTAKE MECHANISM AND EVIDENCE FOR DISSOLUTION

The surface of *Chondrosia* ectosome is characterised by localised concentration of inhalant pores. In experimental conditions, silicate grains dropped on the sponge are quickly carried through specific tracks to these pore-rich areas and incorporated. Small grains (about 250 µm) can be uptaken at the rate of 15 grains/cm^2/day, whereas grains up to 5 mm are engulfed in 3-4 days by progressive envelopment by the ectosome.

Experiments on the *C. reniformis* behaviour towards different substrata and with respect to the uptake of natural and laboratory sands of different mineral composition were also carried out, using:

- natural sand of monocrystalline quartz fragments (grain size between 125-250 µm) purified with chloridic acid;
- laboratory sand (BDH) (grain size between 250-450 µm) with grains consisting of polygonal granoblastic quartz aggregates;
- bipyramidal quartz crystals (about 2 mm);
- chalcedony ground to 250-500 µm;
- opale ground to 250-500 µm;
- coarse- and fine-grained ground rutile;

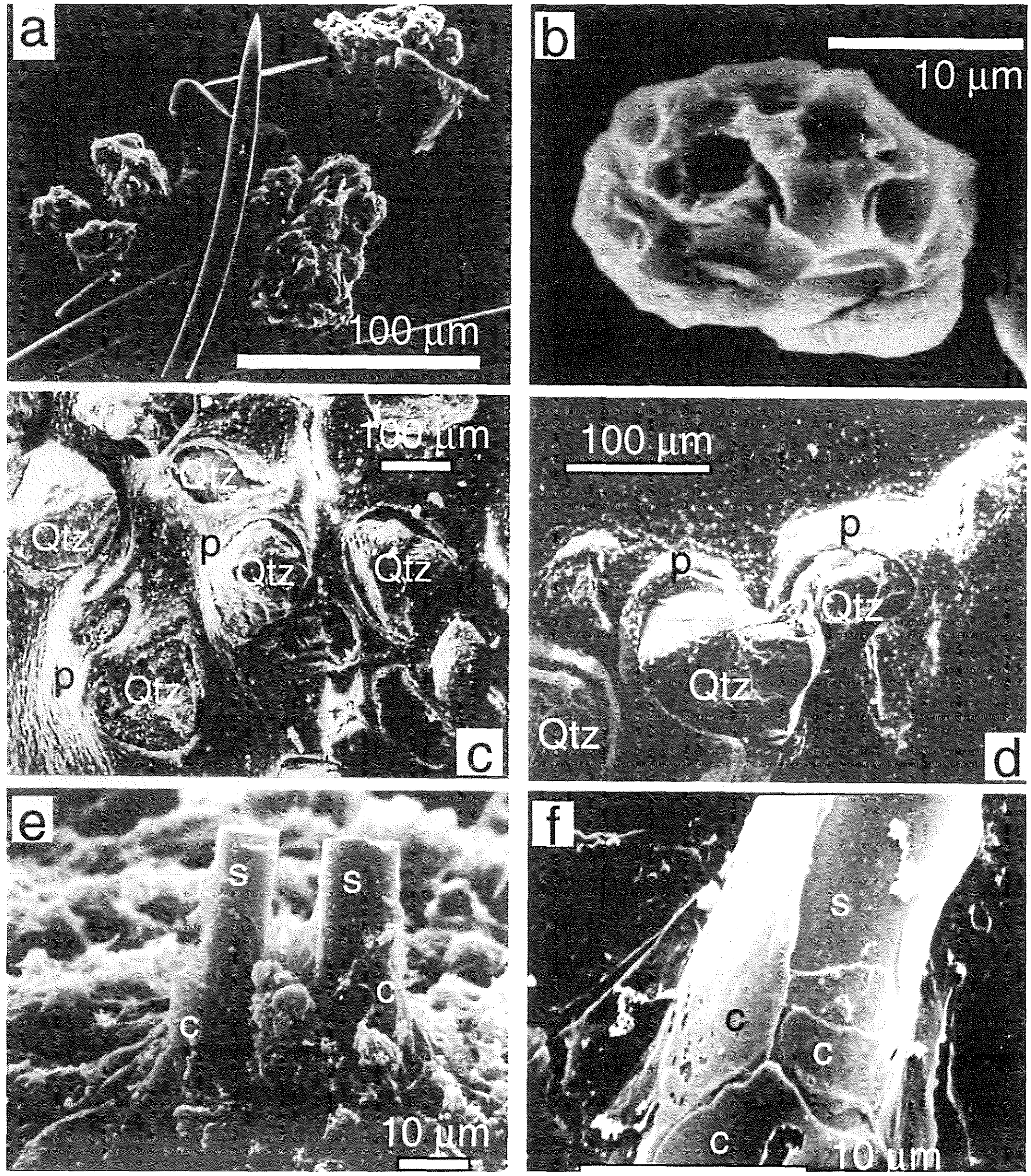

Fig. 2 – SEM micrographs showing: (*a*) Siliceous materials extracted from the ectosome of *Chondrosia reniformis*. Quartz grains are etched, whereas opaline spicules are unaltered. (*b*) The characteristic surface of an etched quartz grain. (*c, d*) Quartz grains (qtz) partially engulfed by pinacocytes (p) at the surface of the sponge; no cells are in contact with the grain. (*e, f*) Opaline spicules (s) progressively covered by the sponge ectosome cells (c) during their incorporation.

– metallic Si grains ground to 250-500 µm.

All the phases were incorporated. Quartz particles, in spite of their mono- or polycrystalline nature, were strongly etched in about 8 days, and brought to the uniform size of 25-50 µm. By contrast, all other phases,

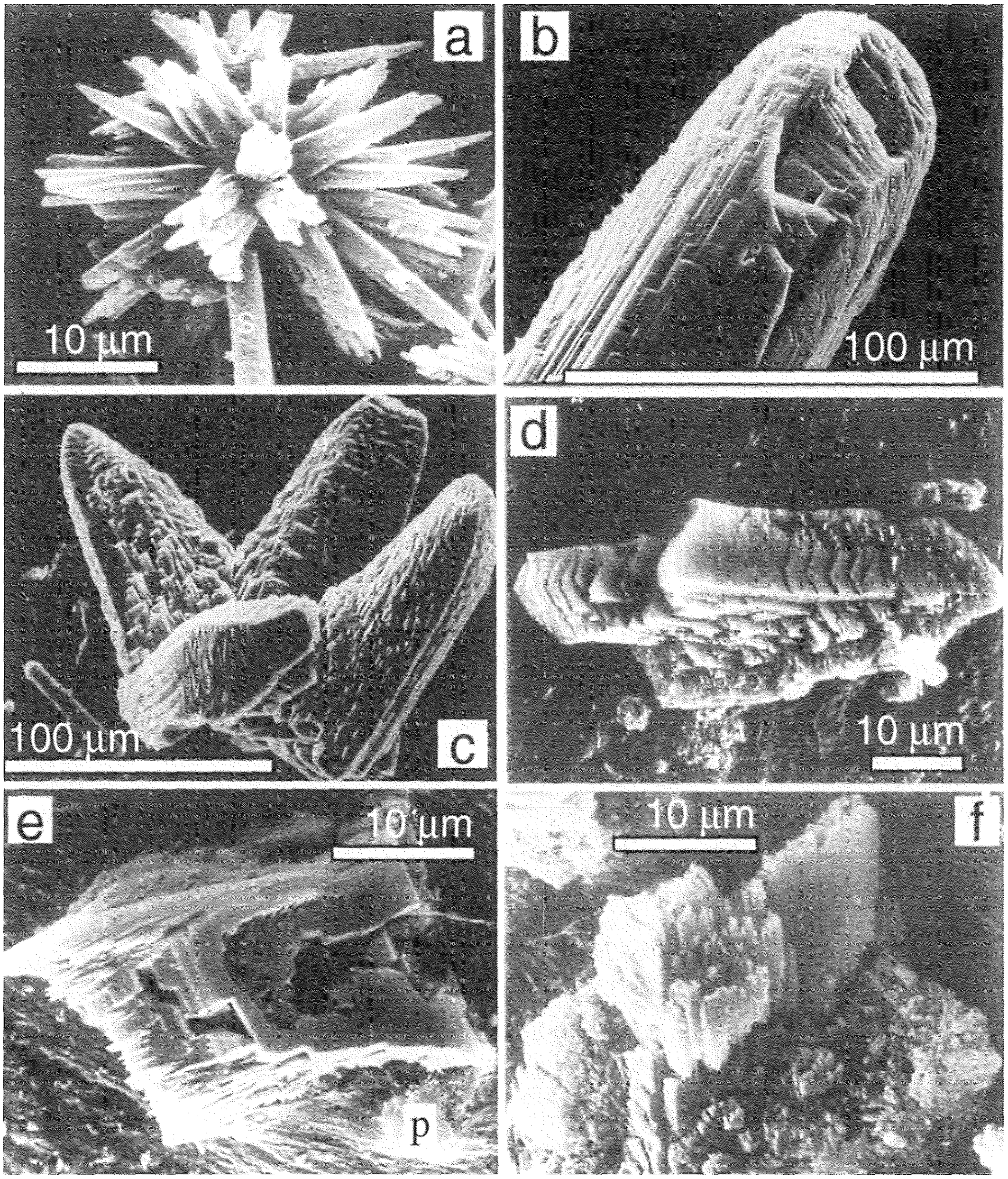

Fig. 3 – SEM micrographs showing calcium oxalates at the surface of the sponge ectosome. *(a)* Radiating aggregates on the sponge ectosome; the opaline spicule (s) possibly acted as nucleation center. *(b, c, d)* Parallel, lamellar aggregates of weddellite. *(e, f)* Parallel, lamellar aggregates of weddellite protruding at the surface of the sponge ectosome. In the *d* to *f* aggregates, the tetragonal simmetry of weddellite is recognizable, with development of dominant {100} and subordinate {001} forms.

included chalcedony and opale, were not modified.

The surface of etched quartz grains is characterised by small (3-5 μm) contiguous conchoidal areas (fig. 2*b*). SiO_2 dissolution is evidenced by a sharp increase in dissolved silica in the water where quartz-treated sponges were reared: in 50 hours, the dissolved silica reached a maximum value of 0.109 mg/l, starting from zero. The grains etched below about 30 μm are probably expelled from the sponge.

Mechanism of quartz dissolution

Quartz can be dissolved by some polyvalent organic, notably citric and oxalic acids (Bennet, 1991). The ascorbic acid concentration in the sponge is high: HPLC analyses showed levels from 1 to 10 μg/g wet weight of sponge tissue. This acid is the reducing agent of proline hydroxilation in collagene biosynthesis by the sponge (Garrone, 1978).

Experiments with 0.5 M solution of ascorbic acid adjusted to pH 7.8 by 0.1 M NaOH at 20°C showed that both quartz and opaline spicules had undergone dissolution (Bavestrello *et al.*, 1995a). Therefore, if the ascorbic acid is the chemical agent for quartz dissolution, this would imply that the sponge interacts selectively with quartz and opale.

Direct observations of the uptake process within the ectosome were carried out on quartz and opaline spicules. Quartz particles were progressively covered by pinacocytes (sponge epithelium cells) forming a ring around the grain (fig. 2*c* and *d*). However, only few cells do directly adhere to the grain. Later, the ring of cells progressively decreases and the grains subside completely within the cortical matrix. In the case of opaline spicules, pinacocytes adhere directly to the grain, which is incorporated by pseudopodial extensions of the cytoplasm (fig. 2*e* and *f*).

On the whole, experiments showed chemical dissolution of quartz, probably promoted by ascorbic and possibly by oxalic acids. However, conchoidal surfaces characterising the etched grains could suggest a concurrent mechanical action responsible for grain size reduction, in analogy with the activity of sponges boring carbonatic substratum (Bavestrello *et al.*, 1997).

Oxalates and gypsum production

The presence of calcium oxalates was first detected in trapped sediments collected close to *Chondrosia* specimens at different depths (10, 15, 25 m) along the Portofino Promontory cliff. Subsequently, they were observed inside the sponge ectosome.

Oxalates are weddellite, $Ca(C_2O_4)\cdot 2H_2O$, and whewellite, $Ca(C_2O_4)\cdot H_2O$, occurring in constant percentages (weddellite 4-6% and whewellite 2-3% of the inorganic material). They are commonly (up to 250/mm^2) observed as grains emerging at the surface of the sponge ectosome, in part covered by pinacocytes. Parallel, radiating or dendritic aggregates (fig. 3) are common and suggestive of high growth rate from oversaturated solutions.

In the trapped sediments, the oxalate percentage varies with depth, but weddellite always prevails on whewellite. In sediments at 10 m depth, weddellite is about 2% and whewellite about 1%; at 15 and 25 m depth, weddellite rises to about 9-10% and whewellite to about 3%.

In the sediments trapped along the Portofino cliff, gypsum was found close to *C. reniformis* populations. This mineral phase is not present in the local sedimentation farther away from the sponge populations, nor in the erosion basin feeding local detrital products.

On the sponge ectosome surface, gypsum is occasionally present as rosettes of radiating aggregates (commonly referred to as «desert roses») (fig. 4) of crystals with tabular pinacoidal habit {010} or, more rarely, as crystals twinned on (100).

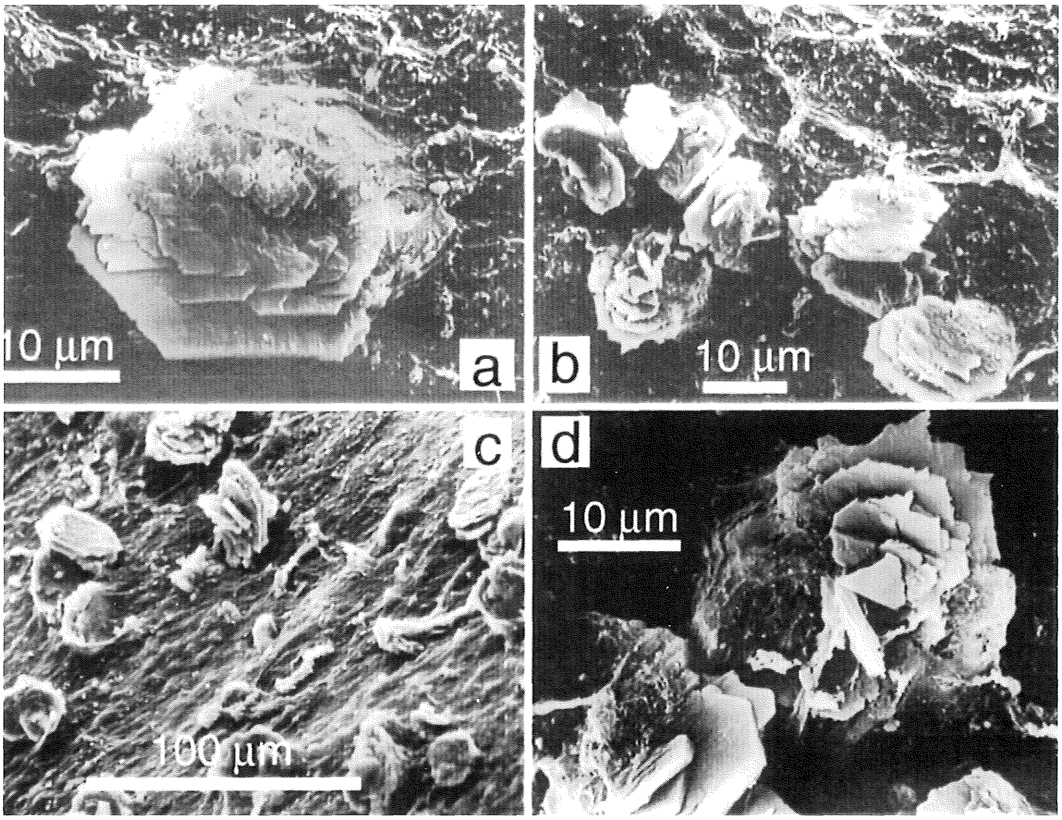

Fig. 4 – SEM micrographs showing aggregates of gypsum crystals on the surface of the sponge ectosome.

DISCUSSION

Ascorbic acid is involved in quartz dissolution by *C. reniformis* (Bavestrello *et al.*, 1995a). This organic acid is the main precursor of oxalic acid in the plants (Franceschi and Horner, 1980), and is correlated to urinary oxalates and calcium oxalate stones in mammals (Roth and Breitenfield, 1977). It turns into oxalic acid in slightly alkaline conditions, like sea water. The release of ascorbic/oxalic acid through the sponge surface is probably aimed to avoid predation or favour the species in the substratum competition.

The presence of calcium oxalates in sediments was recorded only in the Weddell Sea, where weddellite develops in nodules with earlandite, $Ca_3(C_6H_5O_7)_2 \cdot 4H_2O$ (calcium citrate), and interpreted as authigenic mineral of deep water sediments (Lowenstein, 1968). In living marine invertebrates, weddellite was only observed in an Antarctic gasteropod (Lowenstein, 1968) and in a Californian tunicate (Saffo and Lowenstein, 1978).

The presence of gypsum in *Chondrosia* ectosome is surprising. As far as we know, this is the first report of calcium sulphate production by an animal being. The SO_4^{2-} ion is commonly available in seawater, where calcium sulphate is on average dissolved in concentrations of 1.7488g/kg of marine water. In evaporitic processes at high concentrations of SO_4^{2-} ions, carbonates precipitate before calcium sulphates. It can be assumed that these concentrations are attained within the sponge via osmotic processes. The presence of calcium sulphate is sporadic, its production being restricted to particular biological conditions of the sponge.

Discovering the mechanism of biological reactivity of *Chondrosia reniformis* towards different mineral phases controlling selective behaviour could be interesting, for the possible analogies with the pathological processes in vertebrates, such as silicosis and asbestosis.

A different cell reactivity towards different crystallographic forms of silica is well known in vertebrates (Langer and Nolan, 1986). The biological effects of quartz have been related to oxidant properties of crystal surfaces deriving from the generation of silicon-based radicals on the surface and of $(OH)^-$ radicals in the surrounding hydrous environment (Marasas and Harington, 1960). Since such a surface phenomena does not occur on the opale, the difference could explain the behaviour of the sponge towards the two silica polymorphs.

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REFERENCES

BAVESTRELLO G., ARILLO A., BENATTI U., CERRANO C., CATTANEO-VIETTI R., CORTESOGNO L., GAGGERO L., GIOVINE M., TONETTI M. and SARÀ M. (1995a) — *Quartz dissolution by the sponge Chondrosia reniformis (Porifera, Demospongiae).* Nature, **378**, 374-376.

BAVESTRELLO G., CATTANEO-VIETTI R., CERRANO C. and PANSINI M. (1995b) — *Considerazioni sull'ecologia e distribuzione dei Poriferi alle Isole Eolie.* In: F.Faranda *(ed.) Caratterizzazione ambientale marina del sistema Eolie e dei bacini limitrofi di Cefalù e Gioia.* Data rep., *245-250.*

BAVESTRELLO G., CERRANO C., CATTANEO-VIETTI R., SARÀ M., CALABRIA F. and CORTESOGNO L. (1996) — *Selective incorporation of foreign material in Chondrosia reniformis (Porifera, Demospongiae).* It. J. Zool., **63** (3), 215-220.

BAVESTRELLO G., CALCINAI B., CERRANO C., PANSINI M., and CATTANEO-VIETTI R. (1997) — *Distribuzione e modalità di erosione di alcune specie mediterranee di Clionidi (Porifera, Demospongie) associati a Corallium Rubrum.* In: «Biologia e tutela del corallo rosso e di altri ottocoralli del Mediterraneo». Ministero per le Politiche Agricole, Roma, 1999, 115-129.

BAVESTRELLO G., BENATTI U., CALCINAI B., CATTANEO-VIETTI R., CERRANO C., FAVRE A., GIOVINE M., LANZA S., PRONZATO R. and SARÀ M. (1998) — *Body polarity and mineral selectivity in the demosponge Chondrosia reniformis.* Biol. Bull., **195**, 120-125.

BENNET P.C. (1991) — *Quartz dissolution in organic-rich aqueous systems.* Geochim. Cosmochim. Acta, **55**, 1781-1797.

CERRANO C., ARILLO A., BAVESTRELLO G., BENATTI U., BONPADRE S., CATTANEO-VIETTI R., GAGGERO L., GIOVINE M., LEONE L., LUCCHETTI G. and SARÀ M. (1999) — *Calcium oxalate production in the marine sponge Chondrosia reniformis.* Marine Ecol. Progr. Series, **179**, 297-300.

FRANCESCHI V.R. and HORNER T.H. (1980) — Calcium oxalate crystals in plants. The botanical review, **46**, 361-427.

GARRONE R. (1978) — *Phylogenesis of connective tissue.* Karger, Basel 250 pp.

LANGER A.M. and NOLAN R.P. (1986) — *Physicochemical properties of quartz controlling biological activity.* In: Goldsmith D.F., Winn D.M., Shy C.M. (eds.) «Silica, Silicosis, and Cancer: Controversy in Occupational Medicine». Praeger Publ., New York: pp. 125-135.

LLOYD L.L., PARNER F., WHITE C.A. and KENNEDY J.F. (1987) — *Quantitative reversed phase HPLC analysis of L-ascorbic acid (Vitamin C) and identification of its degradation products.* Chromatographia, **24**, 371-376.

LOWENSTEIN H.A. (1968) — *Weddellite in a marine gastropod and in Antarctic sediments.* Science, **162**, 1129-1130.

MARASAS L.W. and HARINGTON J.S. (1960) – *Some oxidative and hydroxylative action of quartz: their possible relationship to the development of silicosis.* Nature, **188**, 1173-1174.

PRONZATO R., BAVESTRELLO G. and CERRANO C. (1998) — *Morpho-functional adaptations of three species of Spongia (Porifera, Demospongae) from a Mediterranean vertical cliff.* Bull. Marine Sci., **63**, 317-328.

ROSE R.C. and BODE M.D. (1995) — *Analysis of water-soluble antioxidants by high-pressure liquid chromatography.* Biochem. J., **306**, 101-105.

ROTH D.A. and BREITENFIELD R.V. (1977) — *Vitamin C and oxalate stones.* J. Amer. Med. Ass., **237**, 101-105.

SAFFO M.B. and LOWENSTEIN H.A. (1978) — *Calcareous deposits in the renal sac of a molgulid tunicate.* Science, **200**, 1166-1168.

TEREGAWA C.K. (1986) — *Particle transport and incorporation during skeleton formation in a keratose sponge Dysidea etheria.* Biol. Bull., **170**, 321-334.