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# CHEMICAL MINORITY ELEMENTS IN BIVALVE SHELLS. A NATURAL MODEL (MAR MENOR, SPAIN)

BY

**Carlos AUERNHEIMER [1], Fernando LLAVADOR and José A. PINA [1]**

## ABSTRACT

The reasons that govern the presence of minority elements in the carbonate exoskeletons has been oftenly discussed by different authors.

The Mar Menor, a coastal lagoon in the SE of Spain presents a high concentration of minority elements in its southern zone.

Shells of bivalves: *Cerastoderma edule glaucum* and *Venerupis aurea* have been analized for Fe, Zn and Mn, showing significant differencies between those that lives in the contaminated zone (South) compared with the ones which do in the northern zone of relatively cleaner watters.

The abundance or scarcity of minority elements in shells of those bivalves is determinated inorganically (in accordance with chemical or crystalographic norms) and the physiology of the organism does not play a decisive role.

## INTRODUCTION

Although numerous chemical analyses of carbonated exoskeletons of marine species have been carried out, and there is abundant bibliographical data on the subject, there remains the question of the interpretation of the factors leading to the inclusion of these minority elements among the calcium carbonate structures.

In some cases, the observations of the various authors suggest that this inclusion should be made on—biological grounds, whilst in others chemical or crystalographic arguments alone are held to be decisive in determining the process.

The Mar Menor, a coastal lagoon in the SE of Spain could sway decisively the balance of evidence owing to the exceptional conditions obtaining there. There is a high concentration of minority elements in its southern zone, and much lower

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concentration in the nothern zone, while the remaining physico-chemical conditions remain homogeneus in the whole extent of the lagoon. This allows us to compare the analyses of the bivalves (*Venerupis aurea* and *Cerastoderma edule glaucum*) (Fig. 1, 2) carried out in both zones for the minority elements analysed (Fe, Zn, Mn).

FIG. 1. — *Cerastoderma edule glaucum*

## THE STATE OF THE PROBLEM

Inorganic calcium carbonate forms crystals of aragonite or calcite, the former precipitating above, and the latter below, 29° C. Minority elements can displace calcium in the structure (Table 1). Small cations are easily displaced in the calcite structure (octahedral coordination) and the larger ones in the aragonite structure (cubic coordination).

The considerable differences in the quantity of these elements contained in the exoskeletons of organisms is normally owing to the aragonite or calcite mineralogical composition of the shell.

In the secretion of the skeleton, the ion must be selected from the water environment, transported to the point of deposition, and concentrated for precipitation,

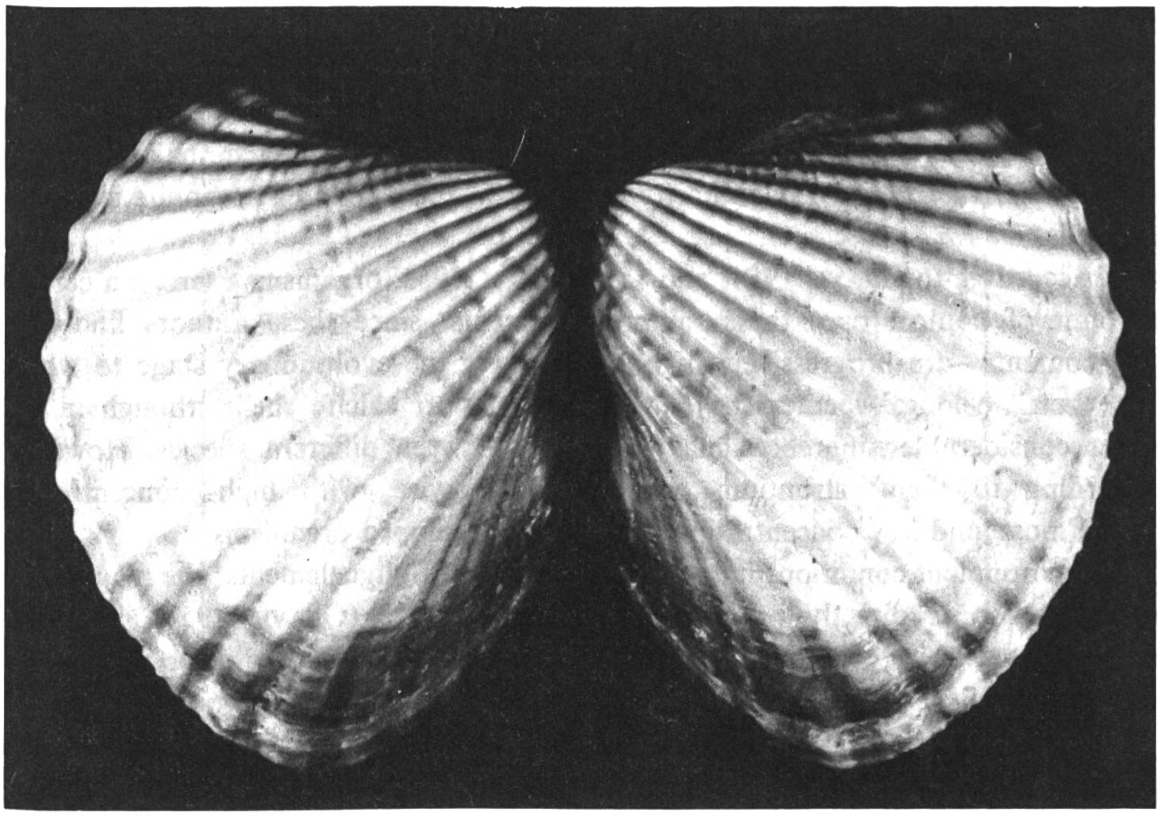

FIG. 2. — *Venerupis aurea*

TABLE 1.

*Ionic radium from cations and coordination.*

| Ion | Ionic radius | Ratio cation radius/0 = radius | Coordination | |
|---|---|---|---|---|
| $Cu^{+2}$ | 0,6 -0,9 | 0,428-0,643 | 6 | OCTAHEDRIC |
| $Mg^{+2}$ | 0,65 | 0,464 | 6 | |
| $Zn^{+2}$ | 0,74 | 0,529 | 6 | |
| $Fe^{+2}$ | 0,76 | 0,543 | 6 | |
| $Mn^{+2}$ | 0,80 | 0,571 | 6 | |
| $Na^{+}$ | 0,95 | 0,679 | 6 | |
| $Cd^{+2}$ | 0,97 | 0,693 | 6 | |
| $Ca^{+2}$ | 0,99 | 0,707 | 6 | CUBIC |
| $Sr^{+2}$ | 1,13 | 0,807 | 8 | |
| $Pb^{+2}$ | 1,20 | 0,857 | 8 | |
| $K^{+}$ | 1,33 | 0,950 | 8 | |

and enzimes must contribute to the process, since the concentration are too low for a strictly inorganic precipitation to occur.

Thus, the process of the formation of an exoskeleton exhibite what we shall call a biological intervention of—the organism, and must, at same time, involve inorganic patterns (crystallographic). To what extent does each make—for the tolerance of the presence of minority elements in the calcite or aragonite structure of shells?

According to CHAVE, 1954; and LOWENSTAM, 1963, organisms exercise a certain amount of control over these minority elements, since these authors find that Mg contents—are progressively higher, the lower the evolutionary stage to which the "taxa" belong, whether they have aragonite or/ calcite shells, though in the latter considerable differences may be found between different species. However, according to them, strontium behaves contrariwise, with high—concentration in the most, and low concentration in the least developed organisms.

Environment conditions influence the presence of oligoelements; the magnesium concentration is directly proportional to temperature (CHAVE, 1954), an effect more apparent in primitive groups, since in more developed invertebrates the Mg content display sligh variations with temperature.

Salinity causes Mg concentration to vary inversely in some species of *Mytilus* (DODD, 1965) and directly in some Echinoids *(Dendraster)* (PILKEY & HOWER, 1960) and Brachiopods (LOWENSTAM, 1961).

Sr contents may also be correlated with temperature—and salinity. In the calcic shells of Crassostrea virginica, Sr increases directly with temperature (LERMAN, 1965), whereas in the Echinoids *(Dendraster)*, which also has a calcite shell, it increases inversely with temperature (PILKEY & HOWER, 1960).

Still more interesting is the case of shells of *Mytilus californianus* and *M. edulis*, for in both species Sr increases with temperature in the outer layer (calcite) and decreases with temperature in the nacred layer (aragonite) (DODD, 1965).

In *Cerastoderma*, the shell of which is formed by two layers of aragonite, HALLAM & PRICE (1968) find higher Sr contents in the inner than in the outer layer, the Sr contents varying, in both layers, inversely with the temperature.

Other trace elements detected in carbonated exoskeleton of invertebrates have not been sufficiently studied. However, a positive correlations of sodium with salinity has been discovered in *Crassostrea virginica* (RUCKER-VALENTINE, 1961).

The relation of the elements in organic carbonates to calcium and to the concentrations in the water can be expressed by the distribution coefficient:

$$\text{Distribution coefficient} = \frac{(\mathrm{M/Ca})\ \text{shell}}{(\mathrm{M/Ca})\ \text{sea-water}}$$

where M and Ca are, respectively, the molar concentrations of the elements considered.

TABLE 2

*Distribution coeficient of diferent cations in bivalves shells.*

| Cations | Distribution coeficient | |
|---|---|---|
| | Calcite | Aragonite |
| B | $10^{-3}$-$2.10^{-3}$ | $0,4.10^{-3}$-$10^{-3}$ |
| Mg | $2.10^{-3}$ | $0,2.10^{-3}$ |
| Ni | 1-4 | 1-4 |
| Cu | 0,4 | 0,3 |
| Fe | 12-26 | 8-34 |
| Zn | 0,9 | 0,3-16 |
| Mn | 15-110 | 5-10 |
| Na | $0,3.10^{-3}$ | $0,2.10^{-3}$ |
| Sr | 0,2 | 0,2-0,4 |
| Pb | 30-600 | 30 |
| K | — | — |
| Ba | 0,3 | 0,3 |

In Table 2, we indicate the values of the distribution coefficient of minority elements studdied in Bivalves from the Mar Menor (Fe, Zn, Mn), as well as some others (Data from MILLIMAN, 1974). All three tend to be concentrated, though Zn weakly so.

To sum up, we may say that the presence of minority elements in the crystal of inorganically formed calcium carbonate is determined by the properties of the crystal surface in contact with water, temperature and pressure (BLATT, MIDDLETON, MURRAY, 1980).

In organic crystals forming part of exoskeletons, the presence of minority elements is attributed by some authors to the originally different mineralogy (aragonite or calcite); by others to environmental conditions (temperature, pressure, salinity); and by others still to a physiological intervention of the organisms as to the acceptance or rejection of these elements.

Finally, it should be added that most authors are inclined to accept a combination of at least two of these three causes.

## PHYLOGENETIC AND PHYSIOLOGICAL OR ENVIRONMENTAL EFFECT?

The phylogenetic effect upon the mineralogy of the shell is determined beforehand, inasmuch as each species is bound to be formed by one of two minerals: aragonite or calcite. Nevertheless, in the chemical composition of these minerals there seems to be an environmental effect, displayed in the grater or lesser absorption of chemical impurities into the mineralogical structure.

This environmental effect, demostrated for local variations in temperature or salinity, acts upon the physiology of the organism, but also upon the inorganic conditions of crystallisation. It would be interesting to test the contents of trace elements of carbonated shells of organisms of the same species—thus avoiding the possible phylogenetic effect (CHAVE, 1954) or different mineralogies—and develop them in the same environmental conditions (temperature and salinity) with only the concentrations of these trace elements in sea-water being varied.

If the organism absorbs more trace elements in environments in which they are more heavily concentrated, and fewer where they are less heavily concentrated, this would show that the organisms are incapable of distinguishing where calcium is concerned, so that the absorption of these elements into the structure would basically take place according to crystallographic norms.

It would be a little as if there were a bricklayer who could only tell approximately the difference between the size of the bricks, but not their colour or their weight. The resulting edifice would appear structurally correct as far as the size of the bricks was concerned, but the colour and the weight would depend on the concentration of bricks of one sort or another that happened to be nearest the bricklayer.

## THE MAR MENOR

Almost ideal laboratory conditions occur in the Mar Menor, for it is a coastal lagoon in which the exchange of wather with the open sea is so slight and the circulatory conditions so restricted, that very similar conditions of salinity and temperature obtain throughout its whole extent.

A number of "ramblas" flow into the southern edge of the lagoon, bringing a high concentration of metallic elements (mainly Fe, Zn and Mn) in their sediments. The weak currents of the lagoon are nor strong enough to disperse these sediments, which thus become concentrated at the discharge points of the "ramblas", whilst the remainder of the Mar Menor is still relatively free of such metallic elements.

At the same time, the lagoon is particularly rich in such bentonic species as the bivalves which are found throughout its extent.

It is therefore to be expected that different contents in minority elements of the exoskeletons of organisms will be due to the greater or lesser distance they live away from the contaminating "ramblas", other conditions remaining constant.

## GEOGRAPHICAL AND GEOLOGICAL CHARACTERISTICS

The Mar Menor is a coastal lagoon with a total surface of 170 km$^2$ and an average depth of 7 m, situated in the SE of the Iberian Peninsula, in the Province of Murcia, and separated from the Mediterranean Sea by a sand bar about 20 km in length with an average width of between 100 and 200 m (Fig. 3).

Communication with the sea is through a series of openings in the sand bar, though the intake of open sea water of the Mar Menor through these gaps is always very low.

Five volcanic islets lie withing the lagoon: Isla Perdiguera, Isla Mayor, Isla del Sujero, Isla Redondo and Isla del Ciervo.

Fresh water enters the lagoon through "ramblas", none of which is situated at the northern end of the Mar Menor. Drainage into the western zone is through a single "rambla", the Rambla de Albujón, whereas there are three feeding the southern end, the three most important watercourses emptying into the Lagoon. These are:

— Rambla del Beal. It flows past, and to the west of, the place knows as Beal, and is fed by waters from the hills south of the plain of Beal, Cabezo de Trujillo, etc. This is the most important of the three "ramblas".

— Rambla de Ponce. It collects waters from the hills lying south of Los Blancos, which disappear in the depressions of the saltpands of Lo Pollo.

— Rambla de Carrasquilla. This flows into the Mar Menor in the form of a delta after its 8 km course in which it collects the rain waters of the plain of El Puntat, to the south of Los Belones.

These three ramblas, lying SW of the lagoon, drain the waters collected from the paleozoic and triassic heights of the Sierra de Portman, south of the Mar Menor, and from the floor of the plain of La Unión, both areas being subject to an intense extractive activity of the minerals Blende, Pyrite and Galena.

## GEOCHEMICAL CHARACTERISTICS

According to SIMONNEAU (1973), generally speaking the coarser fractions of the alluvial deposits brought down with the "ramblas" are formed by goethite, magnetite, and, in lower proportion, hematites and occasionally pyrite (normally oxidised).

The Zn contents of the alluvial deposits varies from 16,300 ppm in the Rambla de Carrasquilla, to 12,800 in Beal and 6,000 in Ponce. Manganese contents are

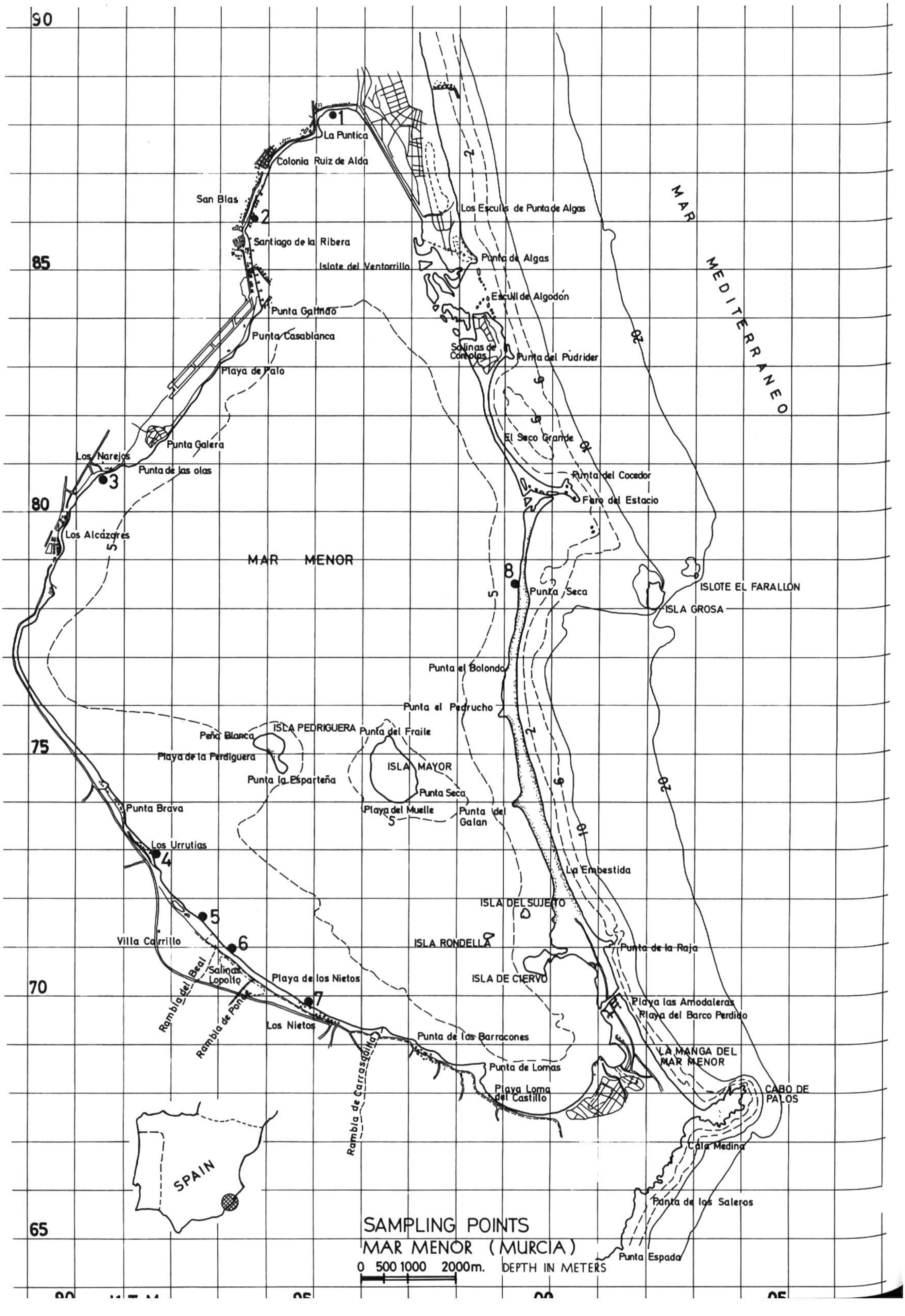

FIG. 3. — The Mar Menor

respectively 10,320, 7,580 and 5,560 ppm. The Fe content accounts for 31% in the Carrasquilla alluvial, and 15,87% in Beal.

The same paper gives maps of isoconcentrations of the elements in the sediments, showing that in the southern zone (our sampling points 5, 6 and 7) zinc shows a concentration above 5,000 ppm; iron shows over 10,000 ppm, and manganese over 5,000 ppm. In the northern zone (sampling points 1 and 2) zinc shows concentrarions under 5,000 ppm, iron under 2,000 ppm and manganese under 500 ppm. Thus, the concentrarions of these elements in the sediments is much grater in the vicinity of the discharge points of the "ramblas", and diminishes as one moves north. The data outlined refers to the fine fraction of the sediment (lutite); concentrations are lower for the coarse fraction (samite).

Variations in temperature between one point and another of the Mar Menor are slight, and even with depth variarion is slight due to mixing caused by the wind.

Ph too does not vary with depth: it oscillates between 7.9 and 8.3, the highest values being found along the south-western edge. Eh, on the other hand, increases from South (75 mv) to North (100 mv).

Chlorinity, on the contrary, increases from north to south, with levels between 27.15 and 28.5 g/l. The average sulphate concentrarion is 2.7 mg/l. We are therefore dealing with a hypersaline environment. In interstitial waters, chlorinity increases to as much as 31 g/l.

The concentrarions of alkaline elements include 15.87 g/l for sodium and 0.53 g/l for potassium, in "free waters", the figures in interstitial waters being respectively 25.3 g/l and 0.98 g/l.

Mn, Fe and Pb contents in "free waters" are lower than 0.05 mg/l, and the Zn reading is lower than 0.005 mg/l.

As for alkaline-earth elements the calcium concentrations is 0.53 g/l, magnesium showing 1.89 g/l.

Magnesium concentrations in interstitial waters are generally in excess of 2 g/l, and in some places are as high as 2.9 g/l. Calcium contents are lower than in free waters.

In interstitial waters, Mn concentrations reach values of between 0.1 and 1.24 mg/l, and are as high as 1.8 g/l in the southern part of the Lagoon and 3.8 at the discharge point of the Rambla de Carrasquilla. Zinc concentrations were fount to be around 0.031 g/l. Lower concentration of this elements (0.009 mg/l) are found in the western zone, whilst in the eastern and central zones we found intermediate values ranging from 0.012 to 0.015 mg/l. The highest zinc concentrations were found at the southwest end, reaching 0.031 mg/l at the discharge point of the Rambla de Carrasquilla.

Fe and Pb contents in interstitial waters remain below 0.05 mg/l.

## METHOD

Given that they are found in abundance throught the lagoon, two species of bivalves were chosen for collection: *Cerastoderma edule glaucum* (Bruguiere, 1789) and *Venerupis aurea* (Gmelin, 1790). These are sedentary organisms, belonging to the endobenthos, inhabiting cavities burrowed into the mud and sand of the sea bed in the littoral zone.

Samples of the two species were taken, and specimens of the same size were selected to ensure that age differences would be slight, thus avoiding the disturbance effect that the geochemical evolution of the Mar Menor might have caused. In addition, live specimens alone were taken to ensure that samples had not undergone transport which migth falsify the conclusion.

Samples were taken from the north end of the lagoon (sampling point 1 & 2) —which is the area furthest removed from the source of contamination—and from the south end (sampling points 5, 6 & 7) close to the discharge points of the "ramblas" which cause the contamination. Samples were also included from the east end (point 8) and from the west end (point 3).

Once the live tissues had been eliminated in the laboratory, any remaining organic matter was destroyed via attack with concentrated $H_2O_2$. Next, the shells were pulverised, dried and dissolved in HC1, and the resulting solution was filtered. The Fe, Mn and Zn contents or this solution were analysed by atomic absorption spectrophotometry.

In thin section, the shells of both species exhibit a structure formed by layers of aragonite.

The outer layer, or "ectostracum" of *Venerupis aurea* display a composed prismatic microstructure, whereas the inner layer, or "mesostracum", reveals a homogeneous microstructure (MAJEWSKE, 1974).

The outer layer ("mesectostracum") and the inner layer ("endostracum") of *Cerastoderma edule glaucum* exhibit a crossedlamellar microstructure (MAJEWSKE, 1974).

The shells of both species are covered by a membrane of a proteic nature, known as the "periostracum".

## Fe, Zn AND Mn CONTENTS OF THE SHELLS

The results of the analyses carried out for the eight sampling points on the contents of the *Venerupis aurea* and *Cerastoderma edule glaucum* shells are shown in Table 3 and are representated graphically in Figures 4-9.

TABLE 3

*Concentrations in ppm of Fe, Zn and Mn in Shells of*
Cerastoderma edule glaucum *and* Venerupis aurea.

*Cerastoderma edule glaucum*

| Sample | Fe | Zn | Mn |
|---|---|---|---|
| 1 | 55.47 | 3.22 | 8.27 |
| 2 | 89.72 | 3.24 | tr. |
| 3 | 92.77 | 9.16 | 50.13 |
| 4 | 129.08 | 11.94 | 45.54 |
| 5 | 827.42 | 95.32 | 287.48 |
| 6 | 950.42 | 22.90 | 111.90 |
| 7 | 152.60 | 23.15 | 48.68 |
| 8 | 62.25 | 4.01 | 0.58 |

*Venerupis aurea*

| Sample | Fe | Zn | Mn |
|---|---|---|---|
| 1 | 43.37 | 3.45 | 5.88 |
| 2 | 60.11 | 6.03 | 4.10 |
| 3 | 56.39 | 11.08 | 33.93 |
| 4 | 369.15 | 39.27 | 144.85 |
| 5 | 338.53 | 47.66 | 100.68 |
| 6 | 4091.58 | 302.51 | 243.01 |
| 7 | 208.33 | 49.45 | 61.99 |
| 8 | 364.04 | 19.13 | 18.35 |

The Fe contents range from 55 to 950 ppm in *Cerastoderma*, and from 43 to 4091 ppm in *Venerupis*. The minimums for both species occur at sampling point 1, i.e. that which is furthest from the area contaminated by the "ramblas". Maximums occurred at point 6, next to the "ramblas".

Zinc varies from 3 (point 1) to 95 ppm (point 5) in the case of *Cerastoderma*, and from 3 (point 1) to 302 ppm (point 6) in the case of *Venerupis*.

As for Mn, we found a range from 8 (point 1) to 887 ppm (point 5) for *Cerastoderma*, and from 4 (point 2) to 243 ppm (point 6) for the *Venerupis*.

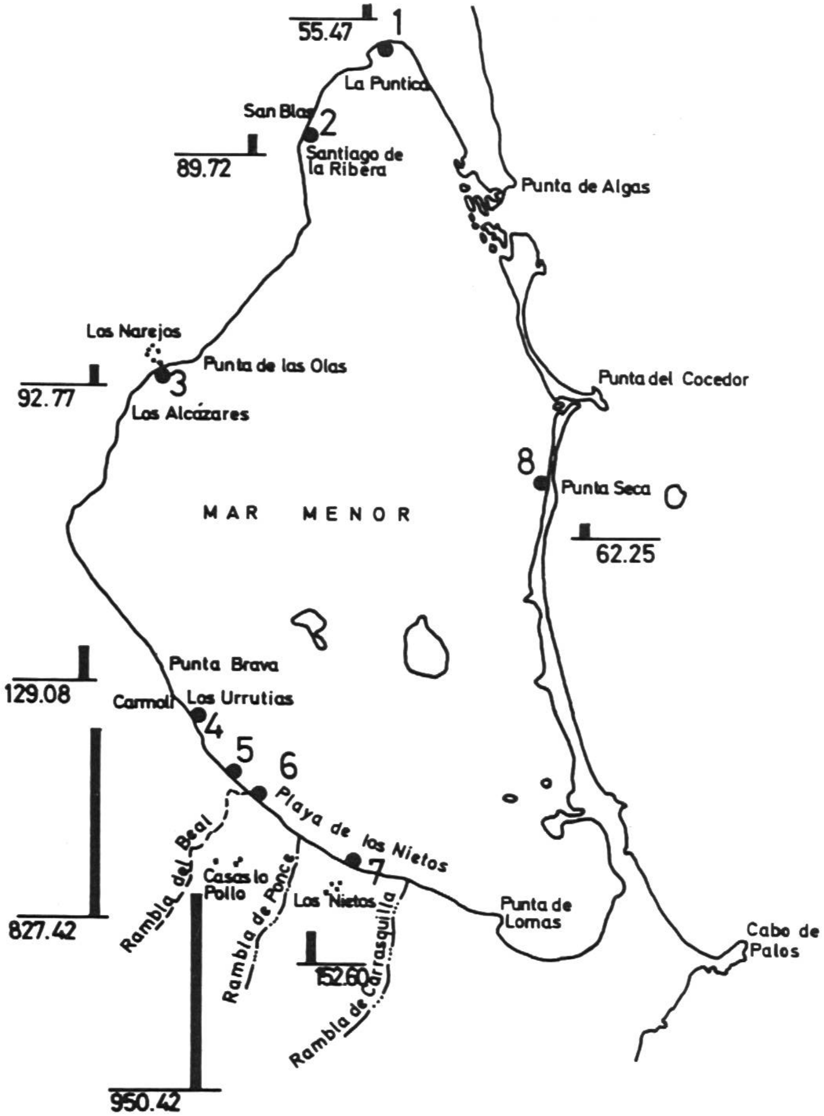

FIG. 4. — Fe content (ppm) in *C. edule glaucum*

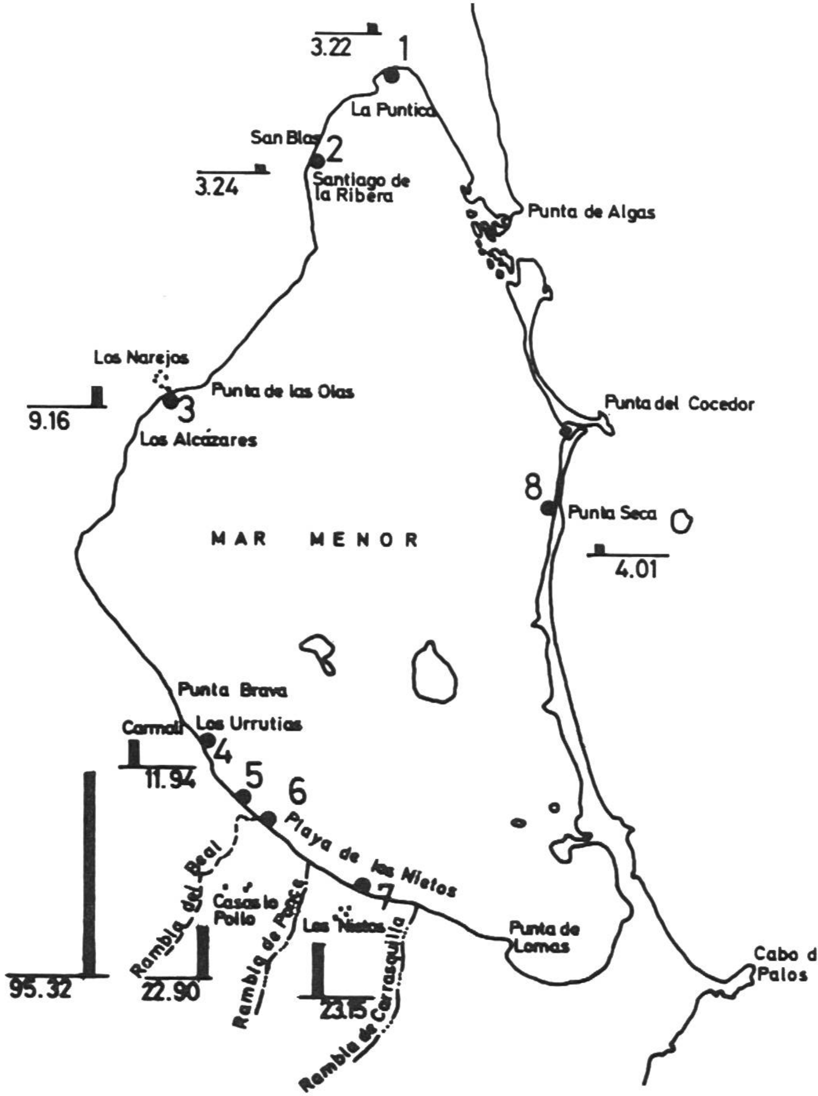

FIG. 5. — Zn content (ppm) in *C. edule glaucum*

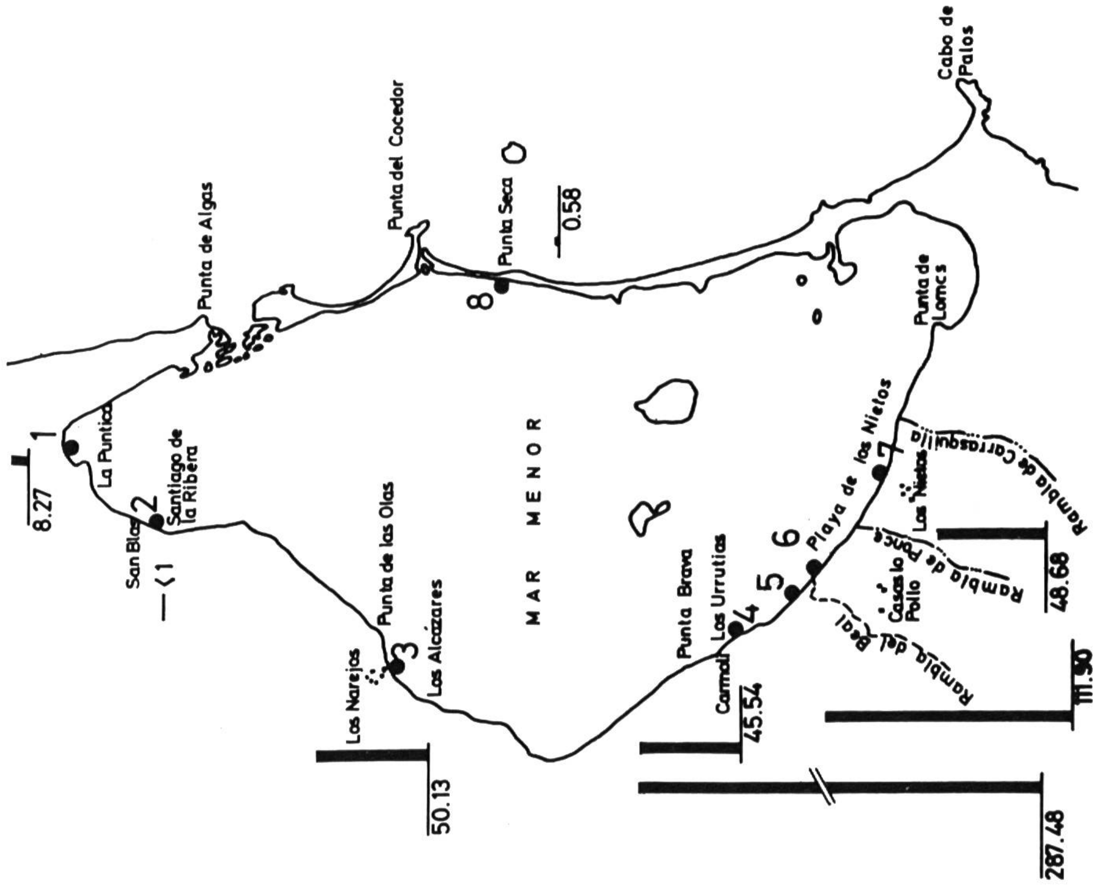

FIG. 6. — Mn content (ppm) in *C. edule glaucum*

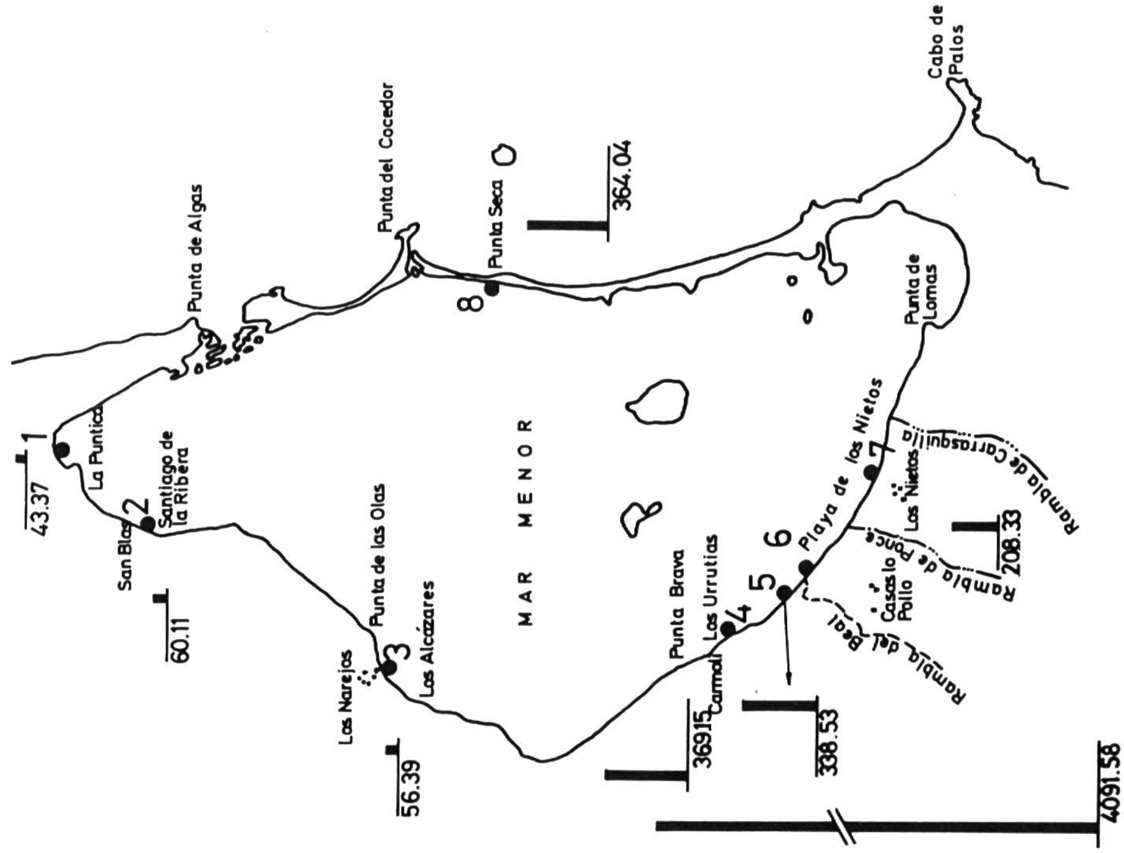

FIG. 7. — Fe content (ppm) in *V. aurea*

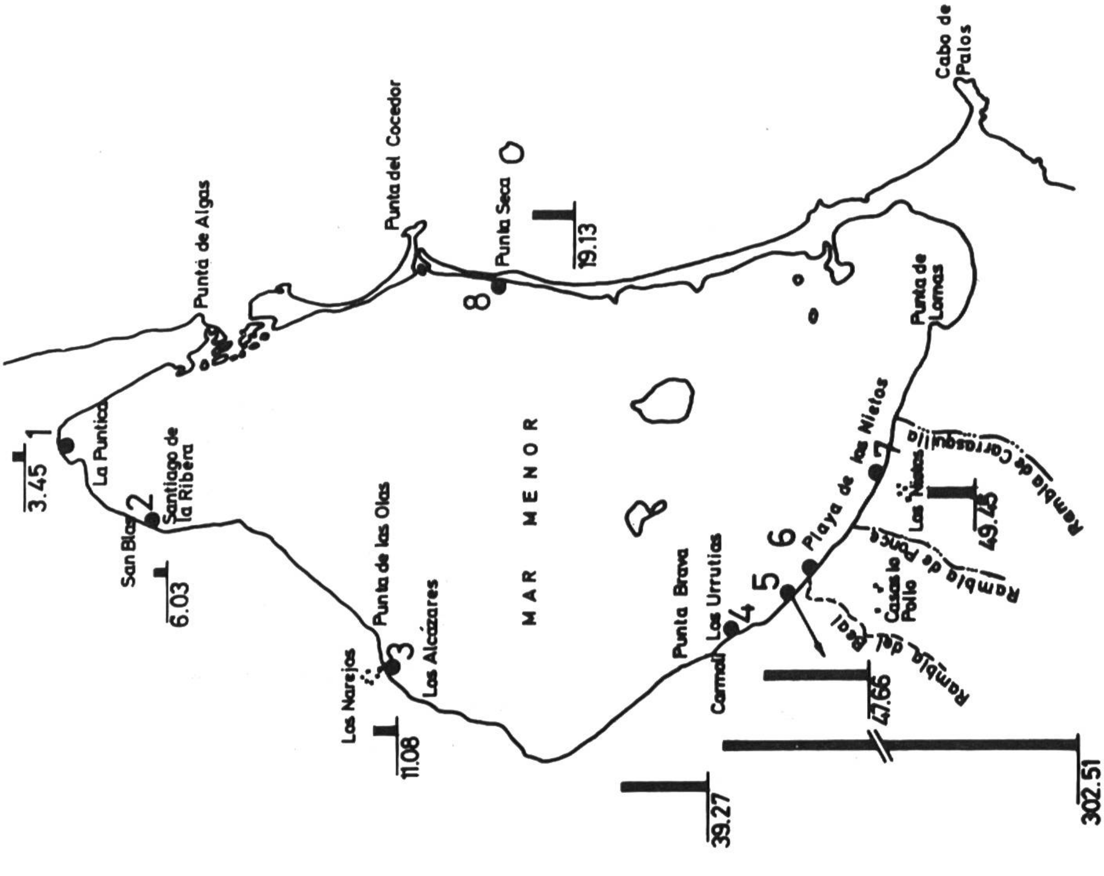

FIG. 8. — Zn content (ppm) in *V. aurea*

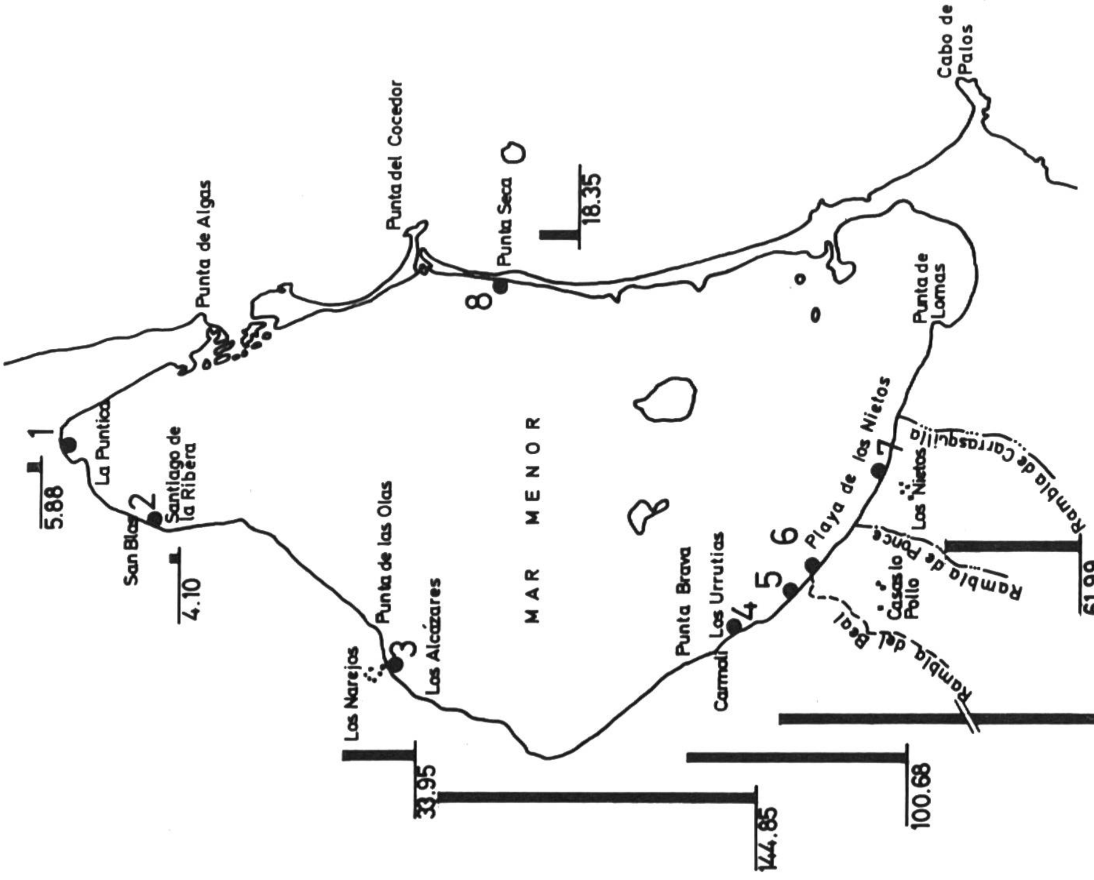

FIG. 9. — Mn content (ppm) in *V. aurea*

## CONCLUSIONS

The three elements analysed display a similarity, inasmuch as minimums are discovered in the area furthest from the source of contamination (points 1 & 2) and maximums nearest this source (points 5 & 6).

The geographically intermediate zones exhibit similary intermediate concentrations.

The contents of these elements in the shells of the bivalves analysed accurately reflects the abundance of these elements in the sea-bed in which they live, or rather the abundance of these elements in interstitial waters. Thus, these organisms are physiologically incapable of rejecting elements in order to avoid their inclusion in their exoskeletons in place of calcium.

The abundance or scarcity of minority elements in the shells of these Pelecypods is determined inorganically (in accordance with chemical or crystalographic norms) and the physiology of the organism does not play a decisive role.

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