EXPERIMENTAL REPLACEMENT OF CARBONATE BY SILICA IN SHELLS

ANTENOR BRAGA PARAGUASSU*

ABSTRACT Laboratory replacement of calcium carbonate by silica was obtained in mollusc shells subjected to acid silica solutions at ambient pressure and temperature.

Results show that no molds are necessary to preserve external form and internal structure in a silicified shell, and that this replacement is possible due to stability in acid medium of organic matter present in shells.

RESUMO Foi conseguida, em laboratório, a substituição de carbonato de cálcio por sílica em conchas de moluscos submetidas a soluções silicosas ácidas, a pressão e temperatura ambientes.

Os resultados mostraram que não há necessidade de moldes para preservar a forma externa e a estrutura interna de uma concha silicificada, e que a substituição é possível graças à estabilidade em meio ácido da matéria orgânica presente nas conchas.

INTRODUCTION Laboratory silica replacement of calcium carbonate in shells was studied using molluscs of living species collected on the northern coast of São Paulo State, in Brazil.

Results demonstrate that a shell submerged in an acid solution of silica at ambient conditions of pressure and temperature can be replaced by silica. During replacement the external form and internal structure of the shell are maintained. Of three experiments performed, two were concerned with the replacement of carbonate by silica and one with the solubilization of shell carbonate in various pH. Chemical and spectrochemical methods were used as analytical procedures.

EXPERIMENTAL WORK Shells, hanging on a thread (Fig. 1A) were placed in distilled water solutions of sodium metasilicate, with concentrations of 31 to 2,000 mg/l of SiO_2. I adjusted the pH of these solutions by trial and error, using HCl, so that a rate of dissolution was obtained that did not allow the destruction of the organic matter network interspersed with carbonate that constitute the structures of the shell. For silica concentrations above 500 mg/l I used pH 2 and under 500 mg/l, pH 2.5. The solution more convenient to observation proved to be 2 g/l of SiO_2 and pH 2, using shells of about 0.5 g.

More intense dissolution of the shells started at their fringes and umbo, turning these regions transparent. Afterwards dissolutions reached the central part of the shell. In Fig. 1B, opaque regions are shown, with a transparent region at the central part of the shell. As the opaque carbonate areas decreased, transparent portions became opacified (Fig. 1C). I was sure that a silica penetration was occurring opacifying transparent regions, because I analyzed similar shells subjected to the same conditions (pH 2 and concentration of 2 g/l of SiO_2) that were at the same phase of the process. After 21 days, most of the calcium carbonate had been mobilized and the shell presented a white tonality across the surface. When opacification became more intense, colloidal silica flocks were visible around the

---

*Departamento de Geologia e Mecânica dos Solos, Escola de Engenharia de São Carlos da Universidade de São Paulo, 13560, São Carlos, SP

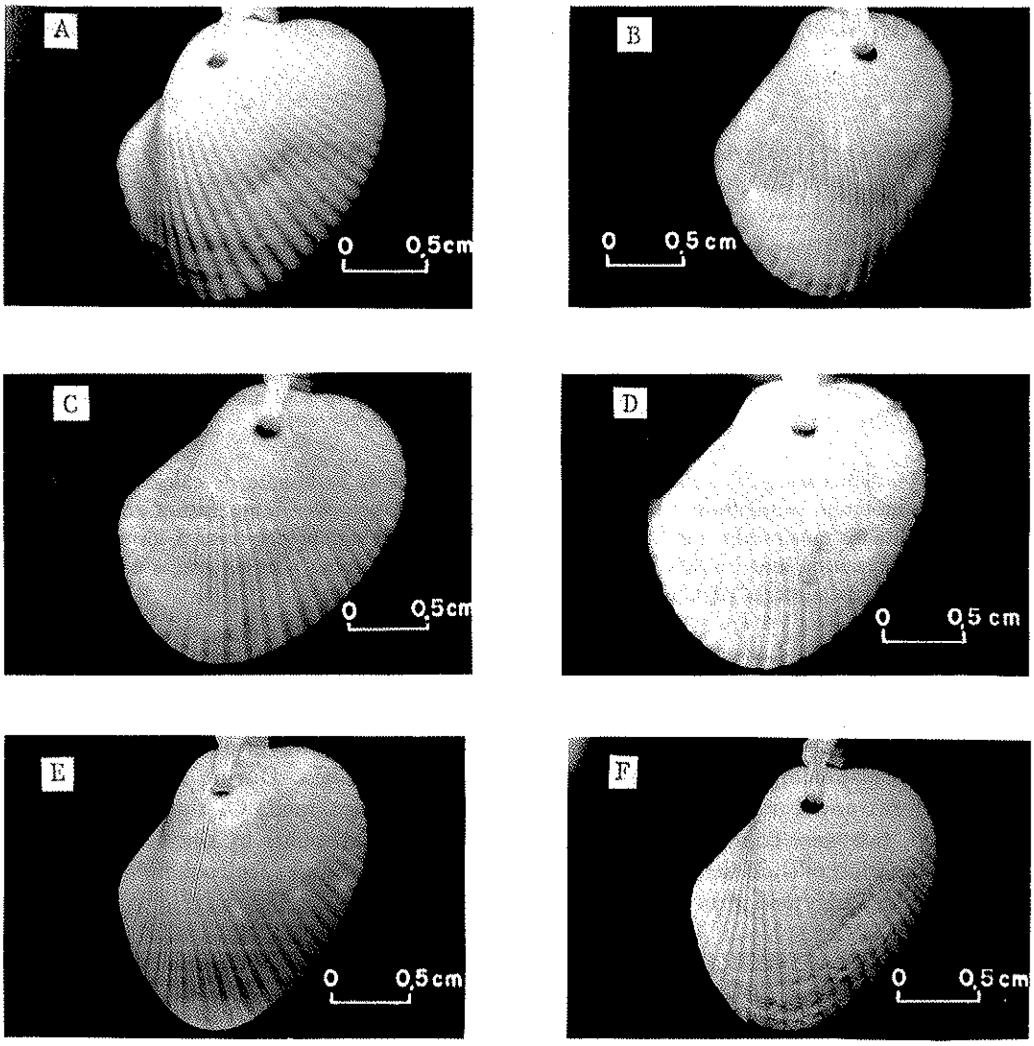

Figure 1 – Shell of *Anadara brasiliana* Lamarck subjected to the replacement process. A, original shell; B, after 10 days; C, after 14 days; D, after 47 days; E, after 3 months; F, after 8 months. Figures A to D are of the shell inside the solution; E, shell outside the solution (hydrated); F, shell dried in air

shell as in Fig. 1D (47 days) due to polymerization phenomena. After 3 months the shell could be removed from the solution without breaking it (Fig. 1E), and a pronounced plasticity was observed, being possible to make thin sections using standard histological methods. The shell was a gel with some coherence. At the eighth month I dehydrated the shell in ambient air and it became whiter, undergoing a small contraction due to loss of water from the gel (Fig. 1F). Forms in this figure and Fig. 1A are identical; Fig. 1F is of a shell constituted of silica and organic matter (conchiolin) without the original calcium carbonate. Its original mass was 550 mg, and after going through the silicification process it was reduced to 54.84 mg, of which 75 % was of silica, the remainder being organic matter and some microelements unmobilized.

Several chemical analyses were made of similar shells subjected to the same conditions. Results show that the silica content increased with time, for example, a shell had its original mass of 380.0 mg reduced after 10 months of reaction to 36.4 mg of which 87% were of silica.

Spectrochemical analyses were also made; Fig. 2 allows a visual comparison that demonstrates element substitution: emission spectrum A (silicified shell) presents very intense Si lines and weakness of Ca lines while, in spectrum B (original shell) Ca lines are evident while Si lines are not present.

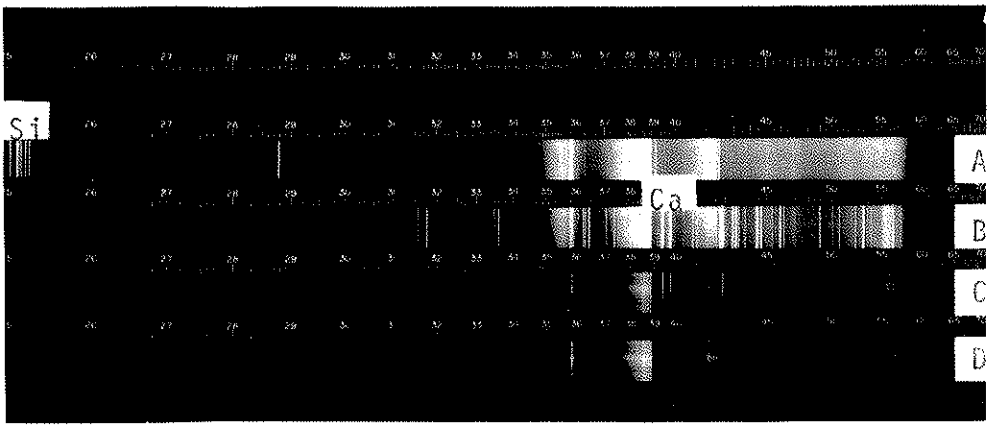

Figure 2 – Emission spectra. A, silicified shell (4 months period); B, original shell; C, calcium carbonate p.a.; D, graphite-electrode

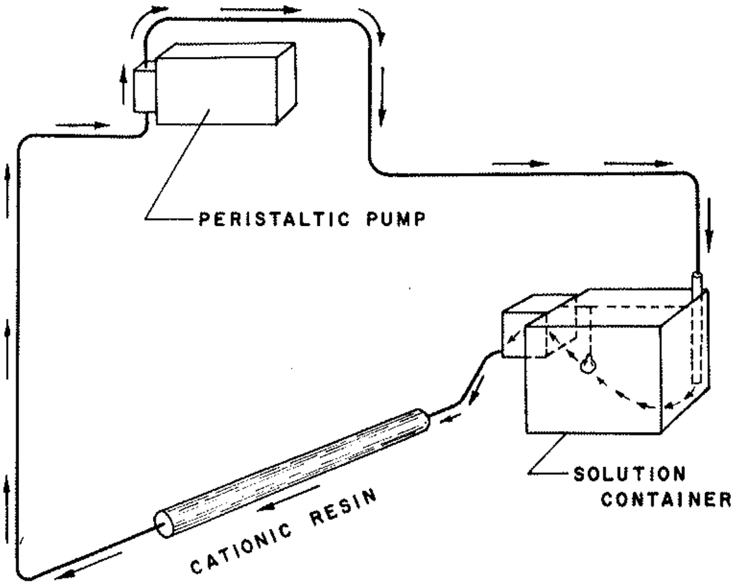

Figure 3 – Solution circulation circuit

Another experiment was made using circulating instead of stagnant solutions because I thought it wise to check whether similar results could be obtained in a situation in which the movement of the solution would alter the polymerization speed of the silica. An apparatus was devised (Fig. 3) so that solution passed around the shell, slowly dissolving the calcium carbonate and carrying the Ca^{+2} to the cationic resin. After extracting the Ca ion, the solution would recirculate, closing the circuit. This extraction intended to avoid a decrease in silica solubility, which can occur (Keller *et al.*, 1963). Results of this second experiment are similar to the first, being the evolution also analogous except that the rate of formation of silica flocks around the shell was slower.

During these two experiments I processed a total of 115 shells, the major part of which was used in chemical analyses of silica and calcium.

In order to speculate about the organic matter which constitutes the internal structures and which, maintaining the external form of the shell during the replacement process, I made several thin sections of silicified shells non dehydrated. I first used specific stains for proteins; these would color, although with difficulty, only the sections of shells subjected to the replacement process for small period of time. Only when I used "Toluidine Blue" was a reasonable contrast obtained because this dye is not specific and reacts with many substances that present acid characteristics. Fig. 4 shows a cross section orthogonal to the a rib of the shell. This shell was subjected to the replacement process for 4.5 months. The configuration of internal layer is not much altered after silicification. In some portions a displacement occurred, however, as a result of the cutting process or to the expelling of CO_2 during the replacement process.

On both experiments I accelerated carbonate dissolution using low pH and designed a new experiment to obtain data about shell solubility in various acid pH. A slice of *Anadara brasiliana* Lamarck was taken parallel to its growth lines from which were detached six fragments, each one with an area of about 70 mm^2 and mass of 50 mg, that were placed in flasks containing solutions of HCl which were maintained at pH 1, 2, 3, 4, 5, and 6, res-

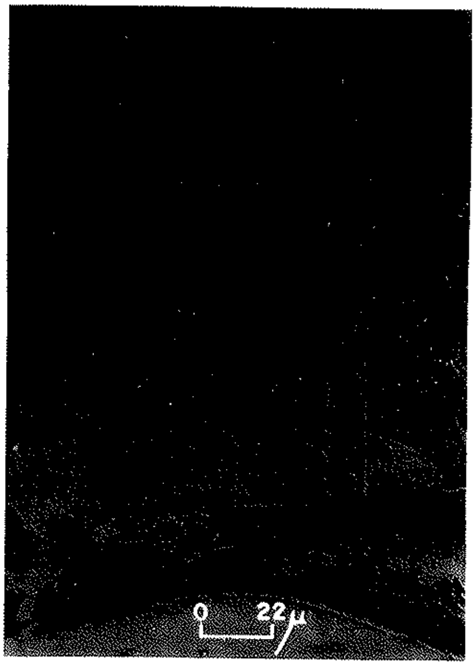

Figure 4 – Ortogonal section to a rib of a silicified *Anadara brasiliana* Lamarck non dehydrated subjected to 4.5 months period of replacement process obtained by standard histological methods

pectively. At time intervals they were taken out and weighted in order to measure the loss of mass. Complete dissolution of the fragments maintained at pH 1 to 4 was obtained during the experiment (415 days). Assuming that the thickness of the fragments is constant, we can consider that the contact surface is proportional to its mass. Measuring mass variation during the experiment (Fig. 5), a dissolution time was calculated for samples in pH 5 and 6. 7.6 and 11.8 years were respectively obtained using the formula

$$t = \frac{1}{K} \ln \frac{P}{P_0},$$

in which P_0 = original mass, P = final mass (my detection limit, 0.05 mg), t = time of dissolution, K(pH 5) = $245 \cdot 10^{-5}$ and K(pH 6) = $160 \cdot 10^{-5}$. Carbonate removal would be completed in about 16 years, for shells of about 500 mg if they were subjected to a solution of HCl with pH 6 (close to the pH measured of natural waters; Paraguassu, 1972).

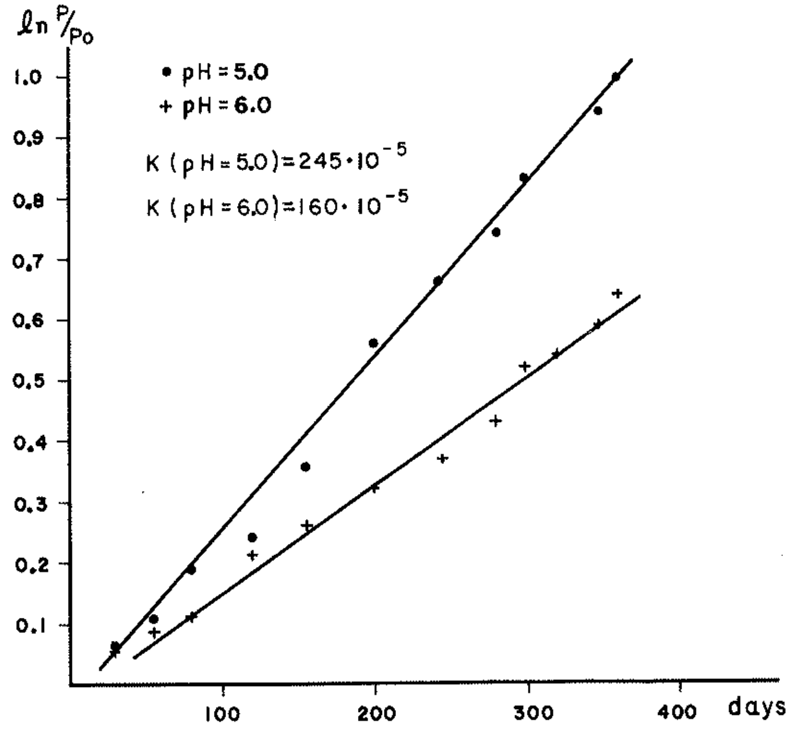

Figure 5 – Experimental dissolution data obtained using a *Anadara brasiliana* Lamarck shell in a solution of HCl

DISCUSSION The major portion of calcium carbonate was removed on the first days of the experiments because, as the reactions evolved, the surface attack of the shell tended to decrease and silica deposition tended to block direct action of the acid as well as the escape of CO_2.

At the conditions of the experiment, the organic matter of the shell seems to have been stable because it is almost insoluble in dilute acid solutions (Hudson, 1967). Silica deposition may be due to the presence of this organic matter, because silica molecules have electrical dipole moments and would be attracted to the organic matter by the centers of electrical charges distributed through the chains of proteins and aminoacids. Retained silica molecules would constitute other centers of charges to retain new molecules, thus increasing the chain. This would also explain the difficulty described in dyeing thin sections of the shell as the period of reaction increased; the first sections were less difficultly coloured because in the initial phase of the replacement process only a small portion of protein was covered by deposited silica. Calcium may also be considered responsible for the silica deposition. During the solubilization of the carbonate, Ca^{+2} ion that enter the solution will favour silica deposition because Ca^{+2} as was mentioned previously may decrease silica solubility.

The drastic weight reduction observed in the dried silicified shells cannot be due only to the difference in densities of calcium carbonate and silica. Because the volume of the shell was maintained during the replacement process, the loss of weight must result from formation of numerous pores. With the evolution of the polymerization process, water present in the shell would leave the colloid and be expelled from the pores, allowing penetration of new silica molecules that might come to fill the shell voids. The rate of polymerization of monosilicic acid is minimum at pH values used on the experiments (Moulik and Ghosh, 1963) being greater at natural pH.

Calcium carbonate dissolution time in pH values found in nature is estimated extrapolating experimental data, but we also have to consider silica deposition to get an idea of the period of time taken by the replacement process in nature. As silica deposition on the shell tends to block direct action of the acid solution, this time is enormously increased.

CONCLUSIONS 1. In order to maintain the external form of a carbonate shell replaced by silica it is not always necessary first to have molds of the shell. Replacement may occur even when the surface of the shell is in open contact with percolating solutions. Rates of carbonate dissolution and silica deposition need not be the same.

2. The replacement may be obtained both by concentrated or diluted solutions of silica.

3. Silica precipitation caused by polymerization phenomena may be favoured by the organic matter and calcium present on the shell.

ACKNOWLEDGEMENTS I am grateful to N. Gandolfi, P. M. B. Landim, A. J. S. Bjornberg, M. Tolentino, and F. S. Germano for helpful discussion and critical reading of the manuscript. Thanks are also due to L. Marino and F. Mattiello for their help in laboratory works, to C. C. Landim for making thin sections, and to J. A. Daccach for mathematical treatment of the results.

REFERENCES

HUDSON, J. D. – 1967 – The elemental composition of the organic fraction, and the water content, of some recent and fossil mollusc shells. Geoch. et Cosmoch. Acta, **31** (12): 2 361-2 378

KELLER, W. D., REESMAN, A. L., and BALGORD, W. D. – 1963 – Dissolved products of artificially pulverized silicate mineral and rocks. Part I. Jour. Sed. Petrology, **33** (1): 191-204

MOULIK, S. P., and GHOSH, B. N. – 1963 – Studies on the effect of temperature and pH on the gelation of silicic acid. Jour. Indian. Chem. Soc., **40** (11): 907-910

PARAGUASSU, A. B. – 1972 – Experimental silicification of sandstone. Geol. Soc. America, **83** (9): 2 853-2 858