

# EXPERIMENTS IN CALCIUM CARBONATE CEMENTATION

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Carbonate sediments may be cemented by a variety of forms of aragonite, calcite, or dolomite. The mineralogy of the cement has been regarded by most investigators as the product of the physico-chemical environment within the sediment at the time of cementation. This has been a reasonable working hypothesis until it was recently demonstrated that many different kinds of cement may occur in beachrocks and in permanently submerged marine sediments. Physico-chemical environmental factors alone cannot explain satisfactorily the distribution of calcium carbonate polymorphs in cements. The possible influence of organic compounds on carbonate precipitation has been mentioned by some geologists, but merely in passing.

There is a considerable volume of published information concerning the biochemistry of the secretion of calcium carbonate in invertebrate organisms. Factors that control the polymorphic crystal formation in calcareous organisms include: (1) the presence of inorganic ions and carbon dioxide (includes pH) (Kitano, 1962; Wilbur, 1960), (2) the presence of organic materials (Gregoire, 1957; Wilbur, 1960), (3) carbonic anhydrase (Stolkowski, 1951; Wilbur and Jodrey, 1955), (4) protein matrix of the shell (Watabe and Wilbur, 1960; Hare, 1961), and (5) temperature (Lowenstam, 1954; Kitano, 1962a).

Kitano (1964) and Kitano and Hood (1965) conducted experiments to determine the effects of organic materials on polymorphic crystal formation. They were successful in precipitating polymorphs of calcium carbonate from artificial solutions by the addition of certain organic compounds such as malate, pyruvate, citrate, succinate, glycoprotein, taurine, chondroitinsulfate and glycogen.

Degens and Matheha (1957), working on the premise that minerals are selective scavengers of organic compounds, investigated the polymerization effects of amino acids on mineral surfaces. They studied sixty different minerals, including carbonates, for their sorption characteristics. Their results indicate that reorganizations on crystal surfaces are accompanied by polymerization of the adsorbed amino acids and that the molecular weight of the polymers can be greater than 10,000.

The foregoing discussion leads the author to believe that we cannot hope to understand the complexities of carbonate cementation until all factors that affect the process are considered. The organic chemistry of the solutions must be examined in addition to the physico-chemical (inorganic) parameters.

Experiments patterned after those of Kitano and Hood (1965) have been conducted at Texas A & M University during the past year. These experiments differ in that they attempted to create an artificial cement within a carbonate sediment rather than a precipitate in a flask. A 7 mm I.D. (inside diameter) glass column was packed with Bahamian ooids that had been autoclaved to remove any

adherent organic substances. During the first experiment only a supersaturated (353 mg/l) solution of calcium bicarbonate was passed repeatedly through the column. After a period of four days the column was clogged and the experiment ended. The column was dried, impregnated with plastic, and thin-sectioned. Thin-section examination revealed prisms of calcium carbonate growing upon the surfaces of the ooids. X-ray analysis of the precipitate showed it to be calcite.

A second experiment was performed using an identical set up but alternately passing two different solutions through the column: (1) a supersaturated solution of calcium bicarbonate (390 mg/l) and (2) a solution containing 6 grams/l of the amino acid taurine and 13.4 grams/l of magnesium chloride. The column clogged after approximately four days. Upon removing it from the system, it was found to be cemented. Following impregnation, thin-sections were prepared and examined. The cement in this experiment is quite different from that created by the first experiment. It appears to be a crystalline cement but not in the form of prisms. The cement occurs at the point contacts between grains and resembles what has been described as meniscus cement. X-ray analyses have not yet been made upon this precipitate, but if the results are similar to those of Kitano and Hood (1965), the cement should be primarily aragonite.

Further experiments will be conducted using other organic compounds and more complex artificial solutions. This paper is intended to be a progress report and to call attention to the fact that carbonate sediments have been cemented in the laboratory under ambient temperatures and pressures. Two different kinds of cement have been created, one under strictly inorganic conditions and the other by addition of an amino acid to the solution.

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