NEWS AND VIEWS

Submarine Lithification of Ancient Limestones

THE discovery of hard, rocky sea beds formed by recent underwater cementation of carbonate sediments (enclosing pottery) is the basis for new thinking on the early lithification of ancient limestones. Limestones are almost pure calcium carbonate sediments (for example, grains of coral and shell debris, oolite) which have been lithified by precipitation of crystals of cement in their pores and by wet recrystallization (calcitization). During the past decade it has been found that extensive lithification can take place in two environments: first, in seawater just below the sediment surface; and, second, in freshwater in sediments exposed to rain and soil waters. Attempts to understand the lithification environments of ancient limestones have led geologists to look at the ways in which the physico-chemical parameters of these environments can be recorded in limestones which were lithified millions of years ago.

There is good evidence that ancient marine limestones began as sediments which were mineralogically similar to those of today. Modern marine carbonate sediments are composed largely of two polymorphs of calcium carbonate—aragonite (orthorhombic) and calcite (trigonal). In aragonite—corals, molluscs and suchlike—strontium substitutes for some calcium; for example, in some living corals strontium is 0.9–1.5 mole per cent (B. F. Spiro, *Bull. Geol. Soc. Denmark*, **21**, 1; 1971). In calcite skeletons—for example, echinoderms, many foraminifera and calcareous algae—substitution of magnesium for calcium is considerable (K. E. Chave, *J. Geol.*, **62**, 266; 1954), chiefly in the range Mg 12–17 mole per cent (the so-called high magnesium calcites). It is known also that lithification of modern carbonate sediments in seawater involves the precipitation of these same solid phases, aragonite and a range of high magnesium calcites (various authors, *Sedimentology*, **12**; 1969). In contrast, lithification in freshwater yields cement crystals of low magnesium calcites (< 5 mole per cent Mg) and causes alteration of pre-existing aragonite and high magnesium calcites, both grains and cement, to low magnesium calcites, including loss of strontium and magnesium (G. M. Friedman, *J. Sedim. Petrol.*, **34**, 777; 1964; W. H. Harris and R. K. Matthews, *Science*, **160**, 77; 1968). The ancient limestones are now purely low magnesium calcite, having undergone final alteration in freshwater. After such a history, what record can these limestones retain of any earlier submarine stage of their lithification?

The late subaerial stages of lithification must, of course, take place by dissolution-precipitation processes in a more or less open freshwater system, because strontium and magnesium are lost. With the microscope it can be seen that two dissolution-precipitation processes have acted (R. G. C. Bathurst, in *Approaches to Paleoecology*, Wiley, 357; 1964): one process involves total dissolution; the other consists in molecule by molecule replacement by dissolution of aragonite and precipitation of low magnesium calcite. Where, for example, this replacement process (calcitization) acts on an aragonitic mollusc shell, relics remain of the intercrystalline sheets of organic matrix, because, as the exchange process is diffusional across a water film, such large objects cannot be flushed

by the pore water. In cements there may be a similar preservation of impurities, originally trapped in the interstices of radiate clusters of aragonite crystals. These impurities can be expected to survive calcitization of the aragonite crystals as radiate patterns of oriented inclusions in the coarser secondary mosaic of low magnesium calcite crystals. Such relic patterns are being found by A. C. Kendall and M. E. Tucker (University of Reading), who postulate a primary aragonitic, and therefore marine, origin for what would have seemed, a few years ago, an obvious subaerially precipitated, low magnesium cement.

In the calcitized mollusc shell the crystallographic orientations of the new low magnesium calcite crystals mimic to some extent the original aragonite orientations. A more exact crystallographic replication occurs in the alteration of echinoderm tests from high magnesium to low magnesium calcite. How this copying takes place is arguable—though it is known in metamorphic rocks (G. Voll, *Liverpool Manchester Geol. J.*, **2**, 503; 1960)—but it should be expected to occur also as a result of calcitization of aragonite cement. This mimetic crystal fabric is just what Kendall and Tucker believe they are finding in low magnesium calcite cements, which must now be supposed began as aragonite. In a recent issue of *Nature Physical Science* (**237**, 43; 1972) R. C. Lindholm described fibrous low magnesium calcite crystals in veins where each fibre is composed of numerous subcrystals with optic axes across the fibre. This anomaly, allied to the unusually high content of magnesium in the low magnesium calcite, suggests derivation from an initial vein precipitate of high magnesium calcite. The radiate pattern of optic axes in radial low magnesium calcite crystals (R. G. C. Bathurst, *J. Geol.*, **67**, 506; 1959) has long been suspected to have an aragonite origin: the work of Kendall and Tucker supports this hypothesis.

P. W. Choquette's analysis (*Science*, **161**, 1130; 1968) of carbon and oxygen isotopes in a finely crystalline low magnesium calcite limestone, partly recrystallized, revealed a positive correlation between the degree of wet recrystallization and the proportions of the lighter isotopes (also C. A. Ross and S. Oana, *J. Sedim. Petrol.*, **31**, 231; 1961). Extrapolation backward of Choquette's data, to the cemented but otherwise unrecrystallized limestone, gave isotopic ratios appropriate to cementation in seawater.

Where the primary solid phase was low magnesium calcite, as in the Chalk of northern Europe, it will have remained unaltered so that its oxygen isotope ratio can even now be used to determine the original ambient temperatures of precipitation (H. A. Lowenstam and S. Epstein, *J. Geol.*, **62**, 207; 1954). Replacement of aragonite and high magnesium calcites by low magnesium calcite, on the other hand, is accompanied by diffusion of ions in freshwater and bulk transport during fluid flow and there is likely to be a substantial but not necessarily total reorganization of the ionic and isotopic content of the original material. It is fortunate that once a limestone has become low magnesium calcite with a porosity of 3 per cent or less, it can resist further changes in the low P–T environment.—From a Correspondent.