

## Etch Patterns on Calcareous Sediment Grains: Petrographic Evidence of Marine Dissolution of Carbonate Minerals

**Abstract.** *Scanning electron microscopy reveals that carbonate grains in sublittoral sediments in the North Sea have surfaces with a microscopic etch relief. In structurally complex skeletal grains, the relief grades into marginal corrosion zones. The etch patterns are caused by dissolution of calcium carbonate, taking place at the shallow sea floor. Carbonate phases affected are calcite, aragonite, and a spectrum of magnesian calcites.*

Vast volumes of the present seas are undersaturated with calcium carbonate, and solid carbonates in contact with these waters are gradually dissolved (1). In theory, the petrographic effects of such dissolution in marine sediments should be obvious since sedimentary carbonate constituents are differentially dissolved because of variations in particle size and form and in crystal solubility (2, 3). In practice, however, the use of petrographic data has been mainly restricted to studies of the opposite process, marine carbonate precipitation, and their potential usefulness for studies of dissolution has been little explored.

In this report I describe minute natural etch patterns on the surfaces of marine carbonate grains. Etch patterns are inherent effects of dissolution and hence categorical morphological evidence of undersaturation. Since they are microscopic topographic features, they are exceptionally well suited for analysis by means of scanning electron microscopy (SEM) (4).

The sediments described derive from depths of 0 to 45 m in coastal waters in the Skagerrak, North Sea (5). The widespread occurrence of etched carbonate grains in these sediments has two implications: (i) microscopic etch patterns may be a generally applicable petrographic indicator of carbonate dissolution, and (ii) considerable marine dissolution of carbonates takes place in the shallow parts of seas at high latitudes.

The carbonate constituents are mainly biogenic. Common skeletal parts are fragments of pelecypods, especially the blue mussel *Mytilus edulis*; gastropods; echinoderms; coralline algae; barnacles; and benthic foraminifers, especially species of *Cibicides*. The dominating carbonate phases are biogenic aragonite and high- and low-magnesian calcite; detrital carbonates, now low-magnesian calcite, are a minor constituent, whereas dolomite is not present.

The natural etch patterns develop on all grain surfaces subject to dissolution. Only fresh skeletal material, still in the form of complete shells and tests, has been found unaffected by the process. The characteristic etch relief is an effect of minor spatial

variations of solubility, variations which reflect heterogeneities in crystal structure and composition in the grain substances. In detrital grains of limestone, the etch topography is clearly related to the faces of the calcite crystal (Fig. 1A), whereas in skeletal grains various calcification units are exposed (Fig. 1, B to D). The ultra-

structures thus revealed in skeletal grains correspond to those known from studies dealing with biologic calcification and shell growth (6).

In single calcite crystals (Fig. 1A), a mature etch topography has a maximum amplitude of 10 to 30  $\mu\text{m}$ , and apparently the amplitude remains constant as the particle dissolves. In structurally complex grains, like mollusk shells, dissolution successively affects deeper parts of the grain, and the surficial etch topographies grade into marginal corrosion zones, hundreds of micrometers deep. Skeletal grains of medium sand size and finer may be affected by dissolution right through the particle fabric.

It is interesting to note that the inter-crystalline organic templates of skeletal carbonates disappear together with, or

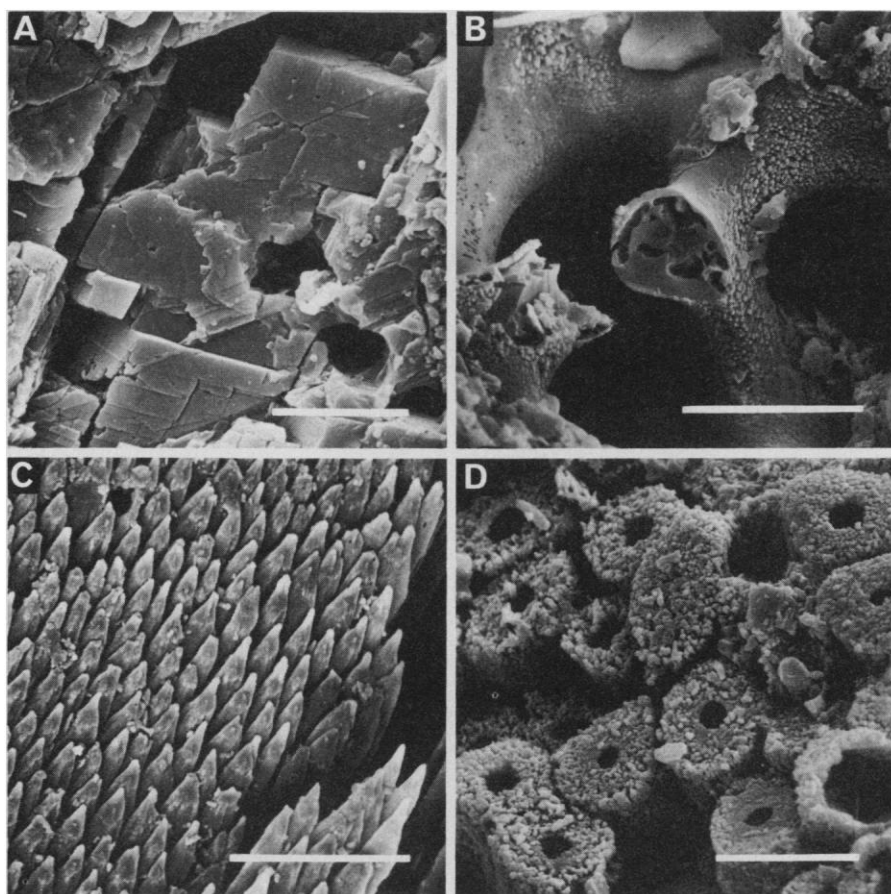


Fig. 1. Natural etch patterns on marine calcareous sediment grains. Scanning electron micrographs; scale bars = 10  $\mu\text{m}$ . (A) Detrital limestone pebble, low-magnesian calcite, water depth 9 m. The surface shown is part of an optically uniform calcite crystal, about 300  $\mu\text{m}$  in diameter (ten times the width in the picture), and the relief is related to various faces in the trigonal calcite lattice. In the lower right are three cavities made by boring filamentous algae. Instrument magnification,  $\times 3000$ . (B) Fragment of mineral part (stereome) of echinoderm, high-magnesian calcite, particle size fraction 125 to 250  $\mu\text{m}$ , water depth 12 m. Echinoderm plates and spicules, which optically behave like single calcite crystals, reveal a complex internal core-and-rind organization during dissolution. Instrument magnification,  $\times 4000$ . (C) *Mytilus* shell fragment, prismatic calcite part, particle size fraction 250 to 500  $\mu\text{m}$ , water depth 30 m. The fibers are partly separated because of loss of organic substance at the grain surface; the pointed tips are a dissolution effect. Instrument magnification,  $\times 4000$ . (D) Fragment of perithallium of the calcareous red alga *Lithothamnium*, high-magnesian calcite, particle size fraction 125 to 250  $\mu\text{m}$ , water depth 12 m. The skeleton consists of cylindrical compartments, about 12  $\mu\text{m}$  in length, 8  $\mu\text{m}$  in diameter, and with terminal pores. In fresh skeletons, the 2  $\mu\text{m}$ -sized crystals in the compartment walls are regular and firmly set in organic substance. Here, they are irregular and partly disconnected. Instrument magnification,  $\times 3000$ .

even slightly before, the mineral substance (Fig. 1, C and D). In the laboratory, even the most friable grains leave an organic "ghost" after dissolution in glutaraldehyde and thus contain organic matter. Yet, intercrystalline organic templates are not seen in the natural etch surfaces. Organic matter is found only as discrete elements, such as pore plates, aperture linings, and films of periostracum. Structurally complex skeletal grains are much weakened by the disappearance of the binding intercrystalline substance.

The sediments contain a range of carbonate phases of varying solubility. Individual particles frequently consist of more than one phase—for example, aragonite and calcite in *Mytilus* shells and a spectrum of magnesian calcites in echinoid skeletons. In the material studied, all varieties of calcite and aragonite are affected by dissolution and thus gradually lost from the sediments. Absolute or relative rates of dissolution are not yet known but exposure experiments are in progress. As a subjective estimate, distinct etch surfaces may form in one or a few years.

In an exposure experiment in the deep sea (3, 7), spheres of optical calcite were etched at a maximum rate of 1  $\mu\text{m}$  per year, whereas specimens of aragonite pteropods and calcite foraminifers were entirely dissolved in 4 months.

Marine calcareous substrates are frequently attacked by boring organisms, such as sponges, algae, and fungi, which remove mineral substance (8). Such bioeroded surfaces are common in the Skagerrak sediments, but they are readily distinguished from etched surfaces; they reflect forms and activities of the excavating organisms, whereas etched surfaces reflect properties of the etched substances.

Shallow marine sediments from supersaturated waters in the Mediterranean Sea and the West Indies, sampled and analyzed in the same ways as the North Sea sediments, do not contain etched grains. During several years of work with warm-sea carbonates, involving hundreds of hours of SEM, I found abundant evidence of precipitation (9) but never an etched surface. It is evident that the two opposite processes, precipitation and dissolution, leave entirely different petrographic records in the sediments.

E. TORBJÖRN ALEXANDERSSON  
*Department of Historical Geology and Paleontology, University of Uppsala, Uppsala, Sweden*

#### References and Notes

1. The earliest observations were made in pelagic sediments by the *Challenger* oceanographic expedition in 1872 to 1876 and described by J. Murray and A. F. Renard [in *Deep-Sea Deposits, Report of the "Challenger" Expedition* (Her Majesty's Stationery Office, London, 1891)]. Since then, in-

- vestigations related to marine dissolution of carbonates have focused on the conditions in the deep sea. For background, see: R. G. C. Bathurst, *Dev. Sedimentol.* **12**, 362 (1971); A. P. Lisitzin, *Soc. Econ. Paleontol. Mineral. Spec. Publ.* **17** (1972); J. D. Milliman, *Recent Sedimentary Carbonates*, part 1, *Marine Carbonates* (Springer-Verlag, New York, 1974), pp. 223–249; J. M. Edmond, *Deep-Sea Res.* **21**, 455 (1974). From a paleontological point of view, dissolution in shallow seawater may be of no less importance, since the greater part of the fossil record consists of shallow marine sediments.
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4. Standard preparation of material is quick and easy: sediments are separated into Wentworth size grades by gentle wet-sieving, rinsed in distilled water, and air-dried. Dry material is sprinkled onto double-stick adhesive tape on top of SEM stubs and coated with gold, preferably in an ion sputterer. Ordinary, even careless, sedimentological routines will not readily produce accidental etch surfaces.
5. The material was collected at the sediment surface by means of scuba diving, mostly at sublittoral stations with considerable wave and current action. The Skagerrak is a cold marine environment at a latitude of 57° to 59°N. The salinity is 30 to 33 per mil, and the maximum surface water temperature is about 20°C in the summer and about the freezing point in the winter. The carbonate content in the sediments varies from a few percent by weight

in terrigenous sands to over 90 percent by weight in skeletal sands. Aspects of carbonate sedimentation in the area are treated in I. Hessland, *Bull. Geol. Inst. Univ. Upps.* **31**, 1 (1943); E. T. Alexandersson, *ibid.* **3**, 201 (1972); *J. Sediment. Petrol.* **44**, 7 (1974).

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## Volcanic Twilights from the Fuego Eruption

**Abstract.** *Striated twilight glows have been observed since 26 November 1974 in New England, indicating the spread of stratospheric dust earlier observed over Arizona. Similar photometric results were obtained from New Mexico and Florida, and twilights in Puerto Rico showed features not hitherto measured. Letters and verbal reports indicate the source to be eruptions of Fuego Volcano in Guatemala between 13 and 23 October 1974.*

Meinel and Meinel (1) noted on 9 and 16 November 1974 colorful twilight glows while flying near the tip of Baja California. Since 21 November, they have observed red twilights and bluish-ashen daylight skies over southern Arizona. The dust stratum, which Meinel and Meinel estimate to be at an altitude of about 19 km, was attributed to eruptions, between 13 and 23 October 1974, of Fuego Volcano (14.5°N, 91°W) in Guatemala. I observed the dust twilights near Boston, Massachusetts, and have obtained measurements from a small network of twilight photometers. This network had been set up to study the latitudinal dependence of seasonal variations of twilights under the then existing background conditions of stratospheric aerosol.

The twilights in the Boston area in the spring of 1974 exhibited a constant or even decreasing color ratio (the ratio of red, wavelength  $\lambda = 0.77 \mu\text{m}$ , to green,  $\lambda = 0.50 \mu\text{m}$ ) after sunset; in June a very slight purple coloration reappeared, probably in the course of the usual seasonal variation. From June until 23 November, most twilights were inconspicuous and ended (at a solar depression angle of 7° to 8°) with a

watery, yellow-orange seam at the solar horizon. However, on 2 November as light cirrus clouds became invisible during twilight, all photometric and visual aspects of a weak volcanic twilight remained. The morning twilight of 11 November also had characteristics suggestive of volcanic conditions.

On 26 November, A. B. Meinel informed me about the dust event, and, as the cloud cover had just cleared up, a few grayish streaks of haze (2° by 10° wide and slightly tilted to the left) were easily visible above the sun at an elevation angle of 15°, 40 minutes before sunset. Many finer streaks appeared, became pinkish at a solar depression angle of 4°, and disappeared later. A golden glow with a red edge was seen the next morning, and, soon after, the eastern sky was covered with a pink film, everywhere billowy and streaked. As the color ratios of some of the photometric measurements before and after the intrusion of the dust show (Fig. 1), the intensity of the glow was exceptionally strong early on 7 December (Fig. 1c), when the sky seemed to be on fire but with hardly any streaks, and early on 11 December, when the sky was very streaked. Although the