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Electron Microscope Study of Microtexture and Grain Surfaces in Limestones

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ELECTRON MICROSCOPE STUDY OF MICROTEXTURE AND GRAIN SURFACES IN LIMESTONES

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ABSTRACT

Electron micrographs of direct-carbon replicas having magnifications of 5400 to 23,500 times reveal in detail the grain size, shape, and packing of the particles comprising very fine-grained limestones. At these magnifications, however, only portions of a few grains in medium- or coarse-grained limestones can be observed. Grain contacts are mostly curvilinear in very fine-grained limestones but are more frequently straight in coarse-grained limestones. The width of the grain contacts varies.

Breakage of limestone by tension produces fractures that follow grain contacts in some places and cross grains in others. Even very fine-grained limestones (micritic limestones) fracture across many grains, and thus cleavage fracturing characterizes tensile breakage in limestones. Shear fracture surfaces are characterized by slip and/or twin lamellae, partial grain cracks, surface grooves on large grains, and a fine dust on some grain surfaces, thought to have resulted from abrasion during fracturing. Some cleavage fracturing also occurs on shear surfaces.

Eighteen electron micrographs illustrate these and other features.

INTRODUCTION

This study is part of a continuing long-range project to discover the relationship between the physical properties of limestone and dolomite and their performance in use as concrete aggregate, railroad ballast, sewage filter stone, terrazzo chips, and building stone. It has long been recognized that such textural

features as size, shape, orientation, and closeness of packing of the grains comprising limestone and dolomite affect their use behavior. For example, the resistance of high-purity limestones and dolomites to deformation (Harvey, 1963) and their thermal expansion (Harvey, 1966) have been shown to be related to grain size. Other textural features of potential significance are the degree and nature of the interlock of the grains comprising the rocks, the amount and character of the grain surfaces, and crystal imperfections such as fluid or other inclusions.

In the study of the above and other related phenomena, the light microscope does not afford sufficient magnification for acute viewing; hence the electron microscope is being used as a primary tool in this study of the microtexture of limestone and dolomite. The electron micrographs included in this report show some of the preliminary results and it is hoped that they will be of interest to students of carbonate rocks and also will stimulate interest in the use of the electron microscope in the study of carbonate rock microtextures. The electron micrographs of limestone and dolomite illustrate four major phenomena: (1) texture and grain surface of tensile fracture surfaces, (2) texture and grain surface of shear fracture surfaces, (3) the nature of grain contacts, and (4) the character of ground and etched surfaces.

Acknowledgments

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Previous Studies

There are few published reports on electron microscopy of limestones. Pfefferkorn (1952) observed the differential solution and etch pits that occur along slip planes and twin planes in calcite. Gregoirie and Monty (1963) reported on lime mud associated with fossil material and described a tightly interlocking mosaic of the crystalline particles of calcite. Kahle and Turner (1964) made replicas of rock and mineral surfaces, including limestones, for electron microscopic study and illustrated an occurrence of subgrain boundaries in microcrystalline calcite cement in the Beulah Limestone of Colorado.

A general survey of electron microscopy of limestones was made by Shoji and Folk (1964). They noted the occurrence of certain distinctive microtextures—cleavage lines on relatively smooth platy surfaces of coarsely crystalline particles, some slightly curved crystal faces, certain elongated and curved welts (.03 to .3 microns long), and aggregates of curving lines and clumps that produce a spongy appearance on the surface.

SAMPLES AND SAMPLE PREPARATION

Six different limestones were selected for this study. They represent a variety of textural types including coarse-, medium-, and fine-grained limestones. One is Ordovician, one is Silurian, and four are Mississippian in age. All sam-

ples are essentially pure calcitic limestones that have undergone various degrees of recrystallization. The textures observed are those characteristic of dense, relatively hard, well lithified limestones.

Tensile fracture surfaces on the limestones were produced by impact with a hammer, by rupture in a three-point bending test, and by splitting in a compression test in which the fracture surface was in line with the direction of loading. Shear fractures selected for study were failure surfaces oriented about 45 degrees to the direction of compressive loading.

To examine the microtexture of ground limestone surfaces, the samples were ground with 1000 grit abrasive on plate glass, washed gently but thoroughly in soap and water, rinsed several times in acetone, and allowed to dry. Some samples were then etched in concentrated formic or acetic acid for 15 seconds or 6 minutes, respectively, and again rinsed in running water and acetone.

Carbon replicas of the limestone surfaces were prepared for study with the electron microscope following the techniques developed by Bradley (1954, 1956). This replication method has proven to be the most satisfactory for electron microscopists, and was the basis for the procedure used by Kahle and Turner (1964) and Shoji and Folk (1964). Direct carbon evaporation on fractured and smoothed surfaces, with subsequent solution of the limestone, and thoroughly washing the carbon replica before mounting on formvar-coated microscope grids yielded the most satisfactory results for this study. To preserve the carbon replica during solution of the limestone, a backing of dental wax was used and subsequently dissolved in xylene. In some cases, the rock surface selected for study was first shadowed with chromium to fill many of the nearly vertical cracks along grain boundaries and pore spaces. This type of shadowing increases the coherency of the carbon replica and frequently yields more satisfactory electron micrographs. However, some shadowing is always produced by the carbon replication process alone, and this is usually sufficient for contrast and surface analysis. The electron micrographs in this report are the reverse contrast of ordinary photographic prints, and thus shadows appear white and highlights appear dark.

When it was desired to preserve the limestone specimen for future study, a two-stage replication method was used, which is described in detail by Shoji and Folk (1964). Briefly, the method consists of making a plastic peel of the rock surface, making a carbon replication of the peel, dissolving the plastic in acetone, and washing the carbon replica in distilled water.

Interpretation of electron micrographs differs, depending on the replication method used. The direct-carbon procedure gives a nearly uniform thick film and projections on the rock surface remain projections on the carbon replica. The plastic peel, however, produces a carbon replica with reverse topography to that of the limestone. Thus, grooves in a rock surface appear as ridges on electron micrographs made with the plastic peel method. Final analysis of the highs and lows of the rock surface is based on the position and shape of the shadows.

RESULTS

Microtexture of Tensile Fracture Surfaces

Electron micrographs of tensile fracture surfaces in very fine- and even-grained limestones (micritic limestones) indicate that the fractures occur not

only along grain boundaries (pl. 1, fig. 1) but also across grains (pl. 1, fig. 2). Only a few of the micritic particles in limestones display cleavage steps. This is in contrast to an abundance of such steps in the coarse crinoidal limestones studied and, in particular, in limestones with sparry calcite cement.

Electron micrographs of a medium-grained clastic limestone, the Ullin Limestone (formerly Salem-Warsaw), are shown in plate 2, figures 1 and 2. This stone has a semisplendent luster, rough fracture, and is a complex mixture of fossil fragments tightly packed in a fine-grained matrix. Figure 1 shows a mosaic of sparry calcite and indicates that the luster on the fracture surfaces is due to the very smooth surfaces of the broken grains. Such smooth surfaces result from cleavage fracturing of the grains. Nevertheless, the fracture surface of the rock is markedly rough and inspection of figure 1 shows this in detail. The fracture surface abruptly changes directions from one atomic plane to another of different orientation. This rough surface may have been formed by multiple nucleation of cracks occurring at or near grain boundaries that spread simultaneously in several directions.

In contrast to this rough surface, propagation of a single fracture appears to have produced the surface shown in figure 2. Here the fracture went straight across three grains producing a planar surface. However, the individual grain surfaces are less smooth than those in figure 1.

In coarse-grained limestone, the size of the grains frequently precludes the observation of an entire grain. A sample of the Kimmswick Limestone, a packed crinoidal micrite, is particularly coarse crystalline, and cleavage fracturing is shown in plate 3, figure 1, where the smooth cleavage surface is interrupted by minute steps on the grains. The cleavage steps are common on tensile fracture surfaces in the medium- and coarse-grained crinoidal limestones studied. The finer grained matrix of the same rock is shown in plate 3, figure 2. The curvilinear grain boundaries and roundness of grain A in this figure are noteworthy. This grain is about 5 microns in diameter.

Microtextures of Shear Fracture Surfaces

Fracture surfaces in limestone produced by shearing may result during crushing operations or in overloaded mine pillars. Some samples undergoing

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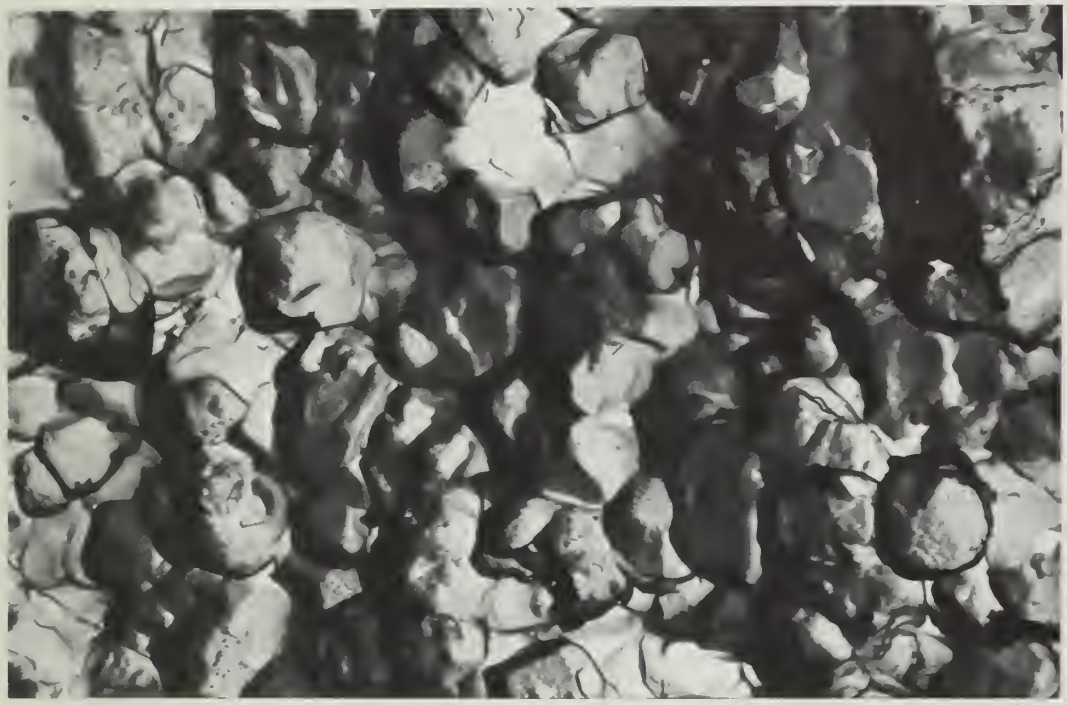
EXPLANATION OF PLATE 1

FIGURE

1 Tensile fracture in fine-grained micritic limestone showing fracture along simple, curvilinear grain boundaries, as well as subrounded grains, and minute nodes on many grain surfaces. The grains are near 3 microns across (direct C-replica, X7200). St. Louis Limestone (Mississippian), Alton, Illinois.

2 Tensile fracture in fine-grained biomicritic limestone showing cleavage fracture across many grains (direct C-replica, X6300). St. Clair Limestone (Silurian), 1.5 mi. NE of Gale, Illinois. (Photograph by Prof. B. Vincent Hall)



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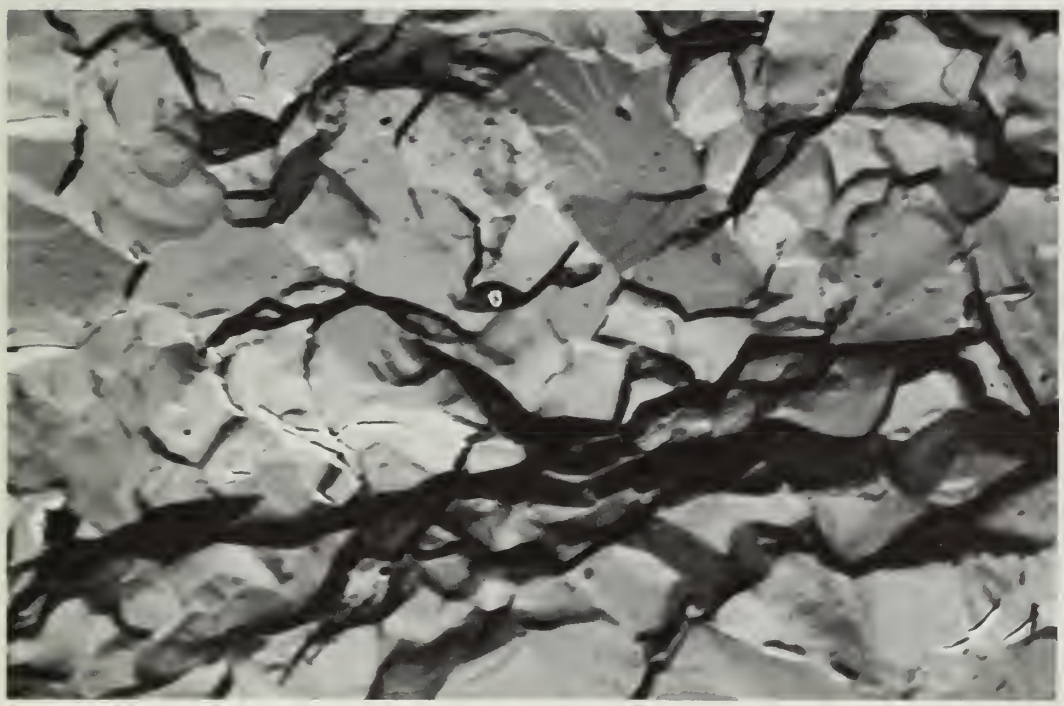

2μ 2

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2μ 2

compressive strength tests fail by shearing. A sample of the Ste. Genevieve Limestone was fractured by shearing during compression, and an electron micrograph of a part of the sheared surface is shown in plate 4, figure 1. The calcite particle in the figure contains slip lines or twin lamellae (indicated by arrows) that were undoubtedly produced just prior to fracture. Other features observed on shear surfaces and not seen on tensile surfaces are extremely fine grains, partial grain fractures, and grooves. Abrasion, or the breaking up of grains into smaller particles along the sheared surface, is responsible for the very fine particle size common on shear fractures (pl. 4, fig. 2). The grain size of the St. Louis Limestone is near 3 microns, as seen on tensile surfaces (pl. 1, fig. 1). However, on shear surfaces of the same limestone, the particle size is reduced to less than 1 micron. Partial grain cracks and chipped edges are seen on some of the larger grains in the same specimen (pl. 4, fig. 3) and are indicative of the source of the very fine powder. Some of the fine powder appears to have been gouged from grain surfaces as a few of the larger grains contain grooves (arrows, pl. 4, fig. 4). Flat troughs bounded by very angular sides, like that occurring near the center of plate 4, figure 4, are not restricted to shear fracture surfaces. Fracture by grain cleavage frequently occurs on sheared surfaces.

Microtexture of Ground Surfaces

Limestone surfaces ground with abrasive (1000 grit) show considerable variation in smoothness. Plate 5, figure 1, shows a smoothed portion of a coarse, crinoidal limestone in which part of the crinoid is rough and part smooth. The smooth part is thought to be a portion of a rim of secondary calcite cement that surrounds a less smooth crinoid fragment. The difference in smoothness is probably related to the relatively high degree of purity and crystalline perfection of the secondary calcite compared to that of the crinoid fragment. Additional relief and distinct grain boundaries are observed on a sample of the Burlington Limestone (pl. 5, fig. 2), which shows a smoothed, etched surface of three crinoid fragments made by the two-stage replication process. In this figure, the grain boundary that appears in the center produced a ridge on the plastic peel, which

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EXPLANATION OF PLATE 2

FIGURE

1 Tensile fracture in medium-grained, clastic, biomicritic limestone showing cleavage fracture in calcite mosaic (direct C-replica, Cr-shadowed, X7200). Ullin Limestone (Mississippian), Jonesboro, Illinois

2 Tensile fracture in limestone showing imperfect cleavage fracture surface and thin, straight grain boundaries (arrows). Note the irregularities on the surface of the grain in the lower right (direct C-replica, Cr-shadowed, X7200). Ullin Limestone (Mississippian), Jonesboro, Illinois.

EXPLANATION OF PLATE 3

FIGURE

1 Tensile fracture in coarse-grained limestone (packed crinoidal micritic limestone) showing cleavage fracture with numerous cleavage steps. Minute nodes occur on certain grain surfaces (arrows). The black spots are carbon (direct C-replica, X6300). Kimmswick Limestone (Ordovician), Thebes, Illinois. (Photograph by Prof. B. Vincent Hall)

2 Tensile fracture in limestone showing relatively wide curvilinear grain boundaries and subrounded grains of the fine-grained matrix (direct C-replica, 10,000). Kimmswick Limestone (Ordovician), Thebes, Illinois. (Photograph by Prof. B. Vincent Hall)

EXPLANATION OF PLATE 4

FIGURE

1 Shear fracture in biosparitic limestone showing slip or twin lamellae (arrows) (direct C-replica, X23,500). Ste. Genevieve Limestone (Mississippian), Cave in Rock, Illinois.

2 Shear fracture of micritic limestone showing minute products of abrasion (direct C-replica, Cr-shadowed, X17,500). St. Louis Limestone (Mississippian), Alton, Illinois.

3 Shear fracture of limestone showing grain cracking (direct C-replica, Cr-shadowed, X7600). St. Louis Limestone (Mississippian), Alton, Illinois.

4 Shear fracture of limestone showing grain grooving (arrows) and grain cracks produced during breakage (direct C-replica, Cr-shadowed, X11,600). St. Louis Limestone (Mississippian), Alton, Illinois.

EXPLANATION OF PLATE 5

FIGURE

1 Smoothed, unetched surface of limestone showing variation in smoothness of a crinoid particle (direct C-replica, X7200). Kimmswick Limestone (Ordovician), Thebes, Illinois.

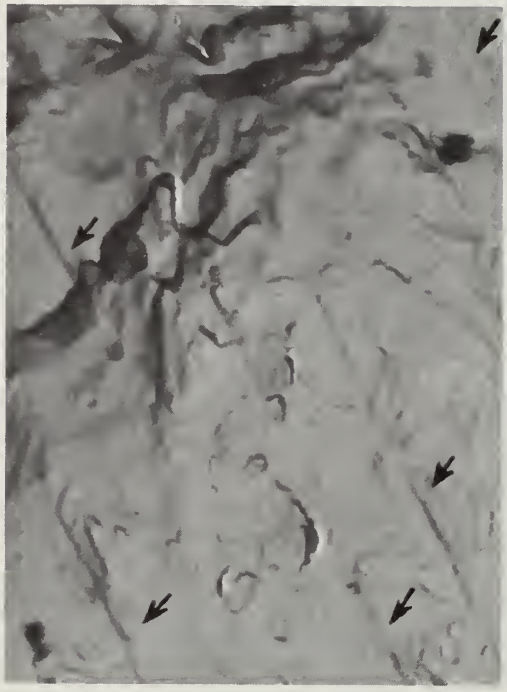
2 Smoothed, acetic acid-etched surface of a crinoidal micritic limestone showing straight grain boundaries as ridges and etch pits as small nodes on the grain in the upper right (two-stage C-replica, X7200). Burlington Limestone (Mississippian), Quincy, Illinois.

2μ

1

2μ

2



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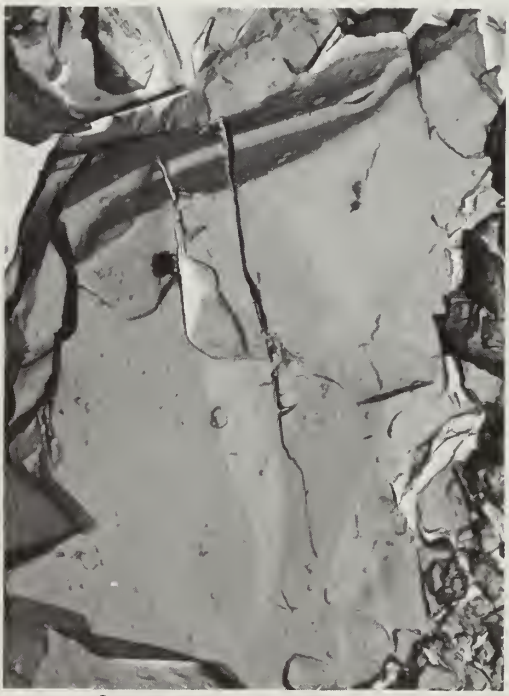

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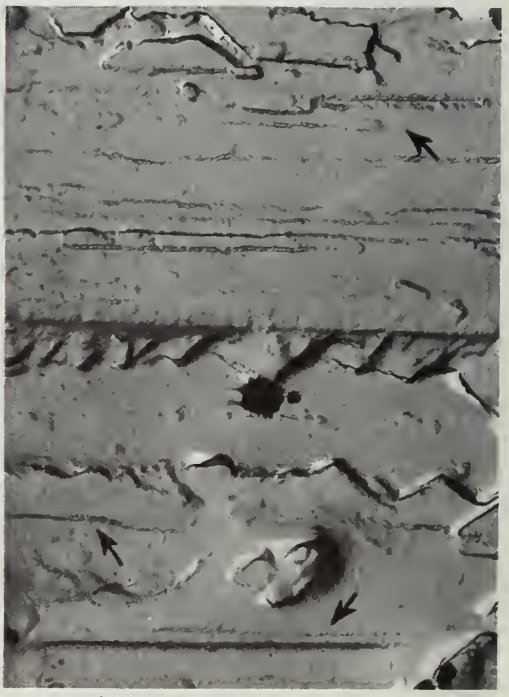

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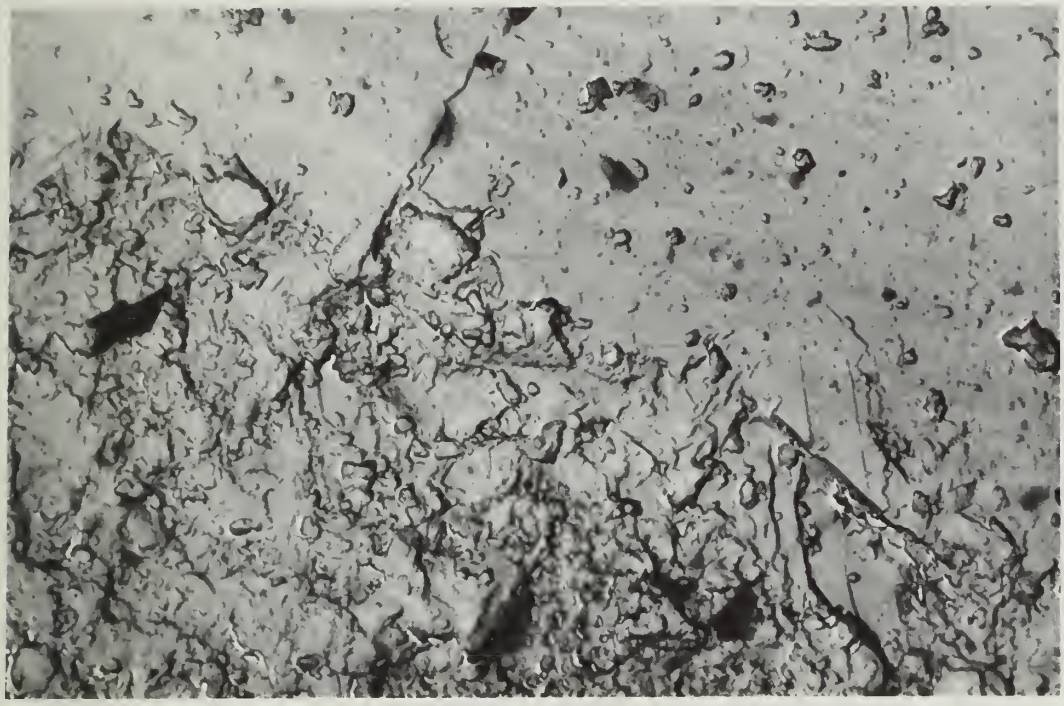

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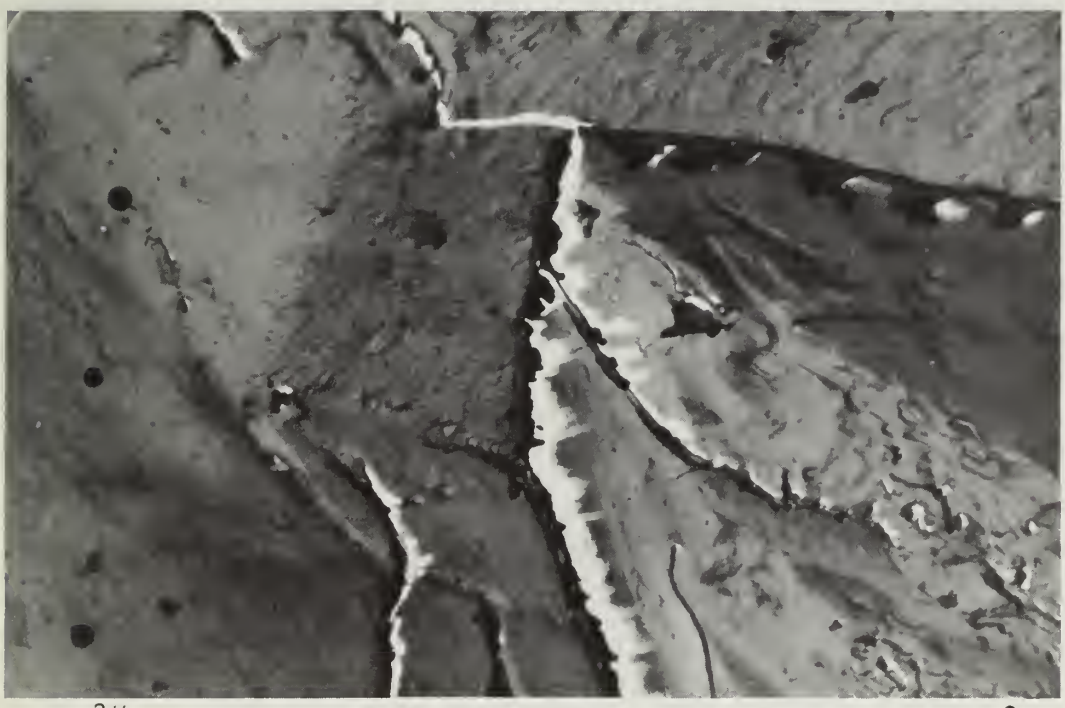

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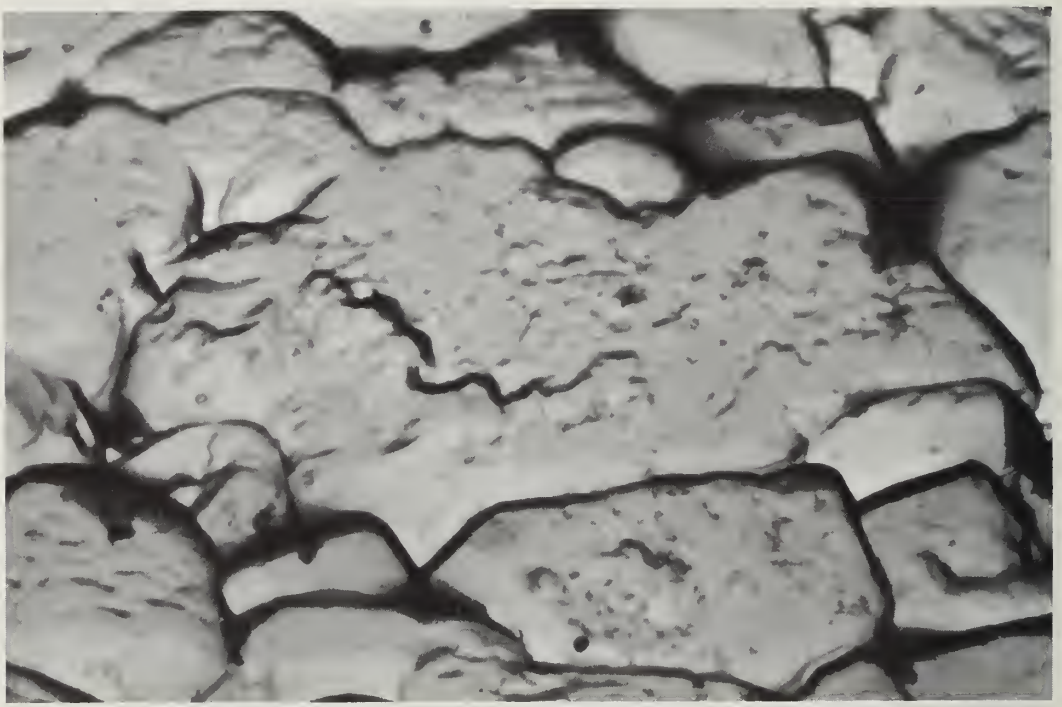

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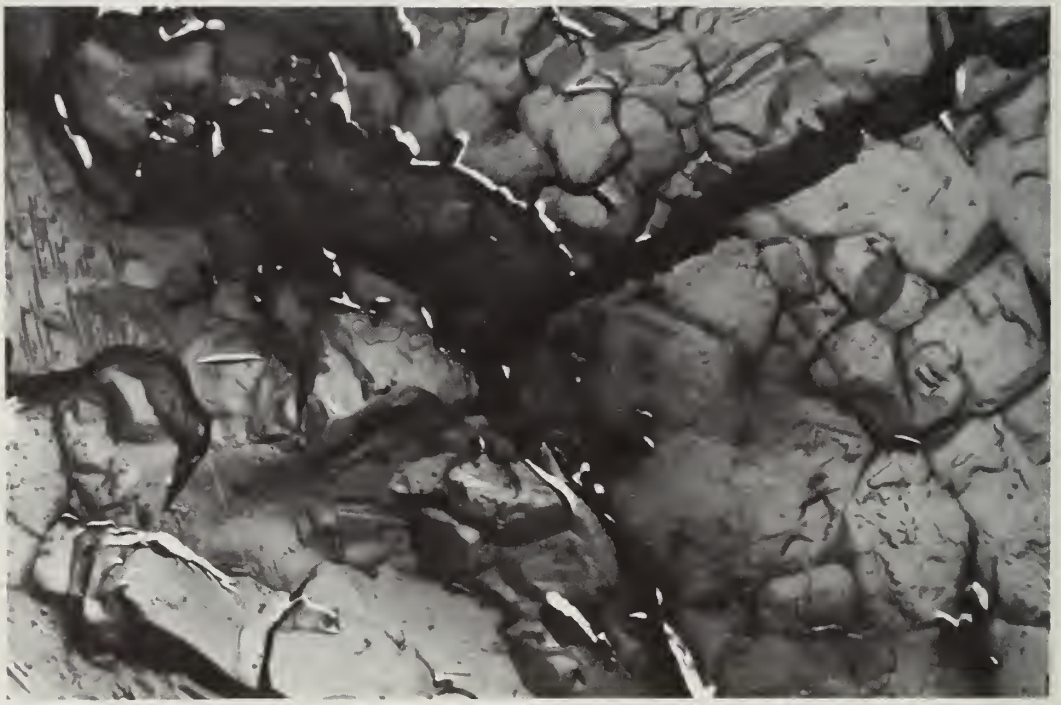


2μ 2

created a light-colored shadow along the boundary during carbon coating. Etch pits are seen as small humps on the grain surfaces.

Grain Contacts

Three principal features characterize the contacts between the crystalline grains composing limestones – their shape, their width, and the nature of the material between the grains. The grain contacts observed with the electron microscope are principally curvilinear, straight, or, in rare cases, serrate. Curvilinear contacts predominate in fine-grained micritic limestones (pl. 1, figs. 1, 2), particularly where the grains are less than about 4 microns in diameter and have a mosaic microtexture. Several contacts in plate 1, figure 1, are concave toward one grain along part of the contact and concave toward the adjacent grain along the remaining part. Curvilinear contacts also occur in the fine-grained matrix of coarse-grained limestones (pl. 3, fig. 2). Many straight contacts, however, characterize crinoidal and other coarse clastic limestones as well as much sparry calcite cementing material with a mosaic texture (pl. 2, fig. 2; pl. 5, fig. 2). In the Ullin Limestone (pl. 6, fig. 1), serrated grain contacts were observed in clastic fossil particles (Brachiopoda ?) in which individual crystal particles are elongated with many in parallel orientation. The contacts are intermediate between curvilinear and straight, and the grains contain many V-shaped protuberances. Such serrated contacts probably were produced by solution and reprecipitation due to ground water.

The width of the grain contacts varies. Two major types are recognized: (1) thin, hairline contacts subsequently described as tight or narrow, and (2) comparatively wide or broad contacts. The wide contacts have a measurable width and many of them contain noncarbonate impurities. The composition of these materials is not determinable by standard electron microscopy, but from examination with the polarizing microscope they are known to vary and include clay, iron oxide, silica, organic material, and/or fluids.

Tight contacts predominate in fine-grained limestones (pl. 1, figs. 1, 2), and many sparry calcite grains have very tight, generally straight contacts between them (pl. 2, figs. 1, 2).

Three large grains having broad, dark-colored contacts are shown in the Ullin Limestone in plate 6, figure 2. Broad contacts also are visible in plate 3, figure 2, and plate 6, figure 1.

EXPLANATION OF PLATE 6

FIGURE

1 Serrate and broad grain contacts in fossil fragment. Note the irregular surface of the particles (direct C-replicas of tensile fracture, X17,500). Ullin Limestone (Mississippian), Jonesboro, Illinois.

2 Broad grain contacts between three large grains containing subgrain boundaries (?) (direct C-replica of tensile fracture, X7200). Ullin Limestone (Mississippian), Jonesboro, Illinois.

Some grains in limestone have a narrow contact where they abut one grain but have a broad contact where they adjoin another (arrows, pl. 2, fig. 2). These differences may be a function of the angle of misfit between their two atomic planes. According to McLean (1957, p. 16), the width of the contact, or boundary separating two grains, increases as the angle of misfit between their atomic planes increases. The wide contacts shown in plate 3, figure 2, and plate 6, figure 2, are not believed to have had this origin, however, but rather are thought to be due to solution by ground water or other geologic factors.

Grain Surfaces

Small, roughly hemispherical nodes are commonly observed in electron micrographs of grain surfaces produced by tensile breakage (pl. 1, fig. 1; pl. 3, fig. 1). In plate 3, figure 1, they occur only on certain crystallographic surfaces. The diameter of the nodes averages about 0.1 micron.

Similar minute nodes were not seen on smoothed and etched surfaces, but larger nodes up to 2 microns in diameter were noted on some secondary calcite grains that are larger than 20 microns in the Ullin Limestone (pl. 7, fig. 1). A random pattern of etch pits was observed on some crinoid particles (pl. 7, fig. 2), whereas a definite pattern of pits and grooves, suggestive of dislocations or minute fluid inclusions, was produced by acid etching of a very fine-grained limestone (pl. 8, fig. 1). Other more irregular surface features are shown on grains in plate 2, figure 2; plate 3, figure 2; and plate 6, figure 1.

The origins of the above phenomena are not understood, but they are not thought to be features created during the carbon replication process.

In the Ullin Limestone, fracture surfaces of dolomite grains, which are distinguished by their rhombic shape, show numerous irregularities parallel to the rhomb surfaces (pl. 8, fig. 2). This fracture pattern is distinct from that shown on the relatively smooth surrounding calcite grains.

CONCLUSIONS

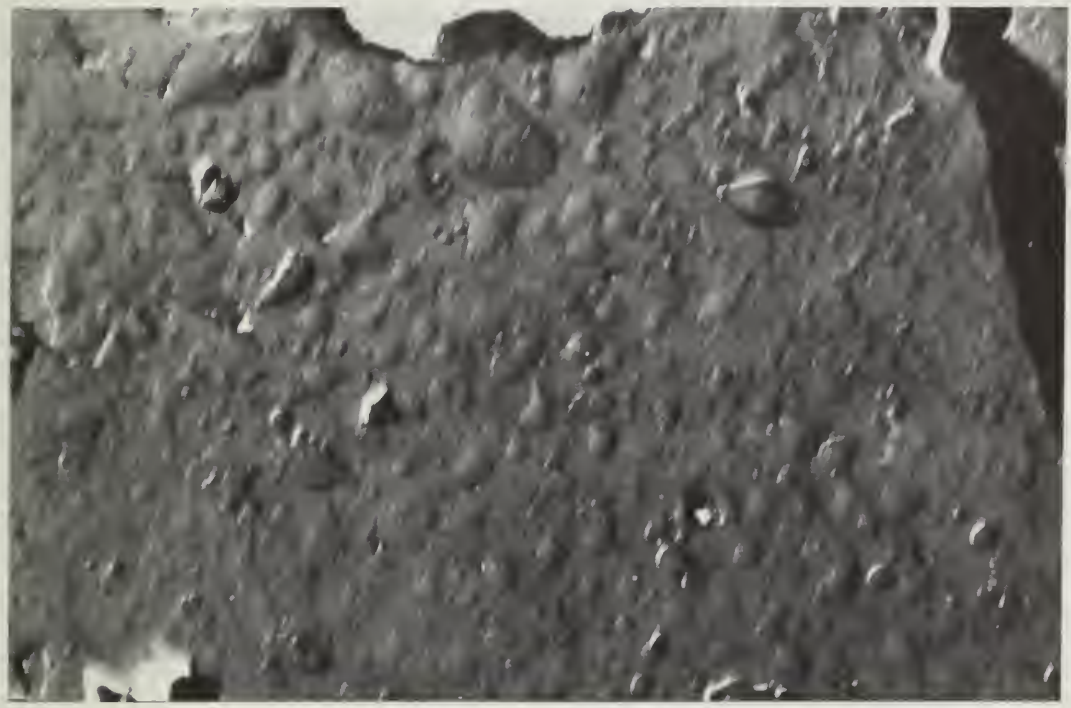
The relative grain size, shape, and packing of fine-grained limestones is clearly indicated by direct-carbon replicas examined with the electron microscope.

EXPLANATION OF PLATE 7

FIGURE

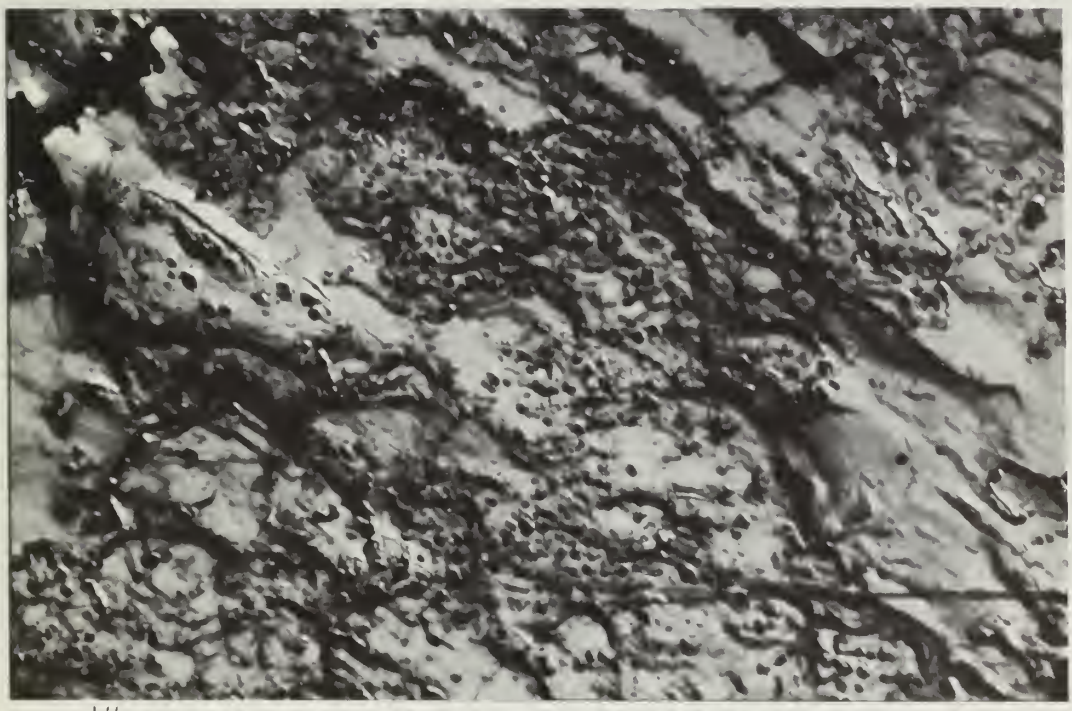
1 Nodes on smoothed, formic acid-etched surface of calcite particle in limestone. The white shadows indicate the features are nodes not depressions (direct C-replica, X7200). Ullin Limestone (Mississippian), Jonesboro, Illinois.

2 Pits on a particle of crinoid in smoothed, acetic acid-etched limestone (two-stage C-replica, X11,100). Burlington Limestone (Mississippian), Quincy, Illinois.



2 μ

1



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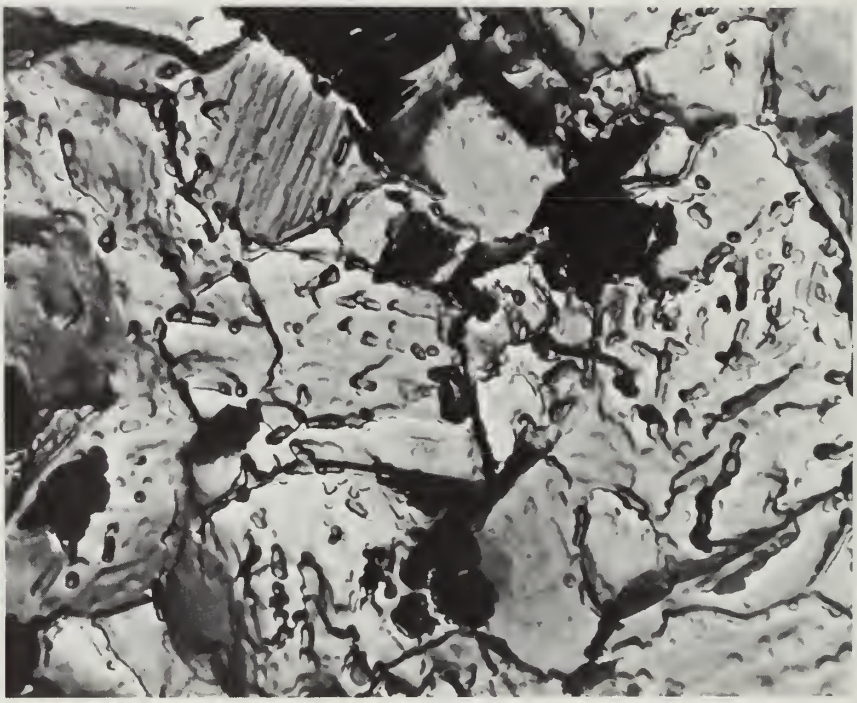

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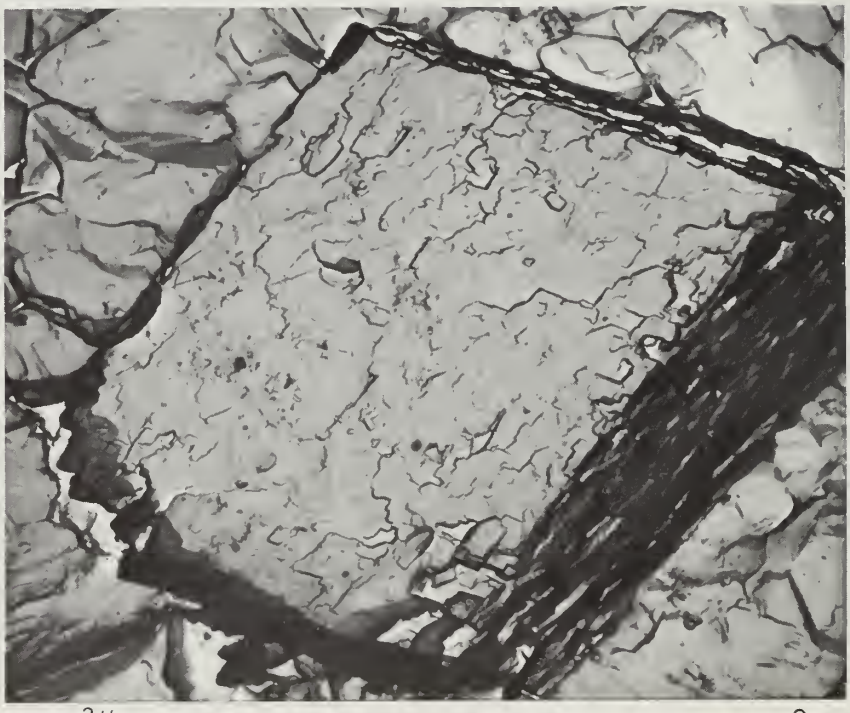

2μ 2

With medium- and coarse-grained limestones, only portions of a few grains can be observed simultaneously with standard electron microscopes. Grain boundaries are notably curvilinear in fine-grained (micritic) limestone, and frequently straight in coarse-grained limestone and in sparry calcite grains with a mosaic texture. The width of the grain contacts appears to vary in part, independent of grain orientation.

Electron micrographs generally make it possible to distinguish grain boundaries from transgranular fractures. Tension fractures in very fine-grained micritic limestone, as well as other types of limestone, occur along grain boundaries in some areas and across grains in others. Tensile fracture surfaces in limestones are characterized by cleavage, particularly in grains larger than about 10 microns, and frequently the cleavages contain minute steps. Shear fracture surfaces in limestones contain extremely fine particles formed by abrasion of grains on the fracture surface, slip and/or twin lamellae on a few grains, partial grain cracks, and grooves on surfaces of large grains. Due to the brittle nature of limestones at ordinary temperature and pressure, cleavage fracture of many grains also occurs on shear fracture surfaces.

EXPLANATION OF PLATE 8

FIGURE

1 Etch pits on fine-grained calcite (micritic) in limestone (direct C-replica of smoothed surface, etched with formic acid, X7200). St. Clair Limestone (Silurian), 1.5 mi. NE of Gale, Illinois.

2 Dolomite rhomb and adjacent calcite grains on tensile fracture of limestone (direct C-replica, Cr-shadowed, X5400). Ullin Limestone (Mississippian), Jonesboro, Illinois.

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