ACID ETCHING IN THE STUDY OF LIMESTONES AND DOLOMITES

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ETCHING TESTS are quickly and easily made, require little apparatus, and give valuable data on the texture, grain size, distribution and nature of noncarbonate materials, and other lithologic characteristics of calcareous rocks, especially limestones and dolomites. In many respects they take the place of thin-sections but have the advantage of requiring little skill to make, of affording a much larger area for study, and of revealing impurities in three dimensions. They also serve to clarify obscure phenomena in thin-sections.

Information from etched specimens, particularly that relating to the nature and distribution of noncarbonate materials, has important practical significance in connection with studies of abrasiveness, structural soundness, and weather resistance. In the study of diagenetic and other changes which have affected limestones, etching tests can be used advantageously. They also aid in lithologic studies relating to stratigraphy and possibly in revealing obscure structures of fossils.

The etching of limestones with acids seems such an obvious procedure that a considerable literature might be expected on its application to calcareous rocks. Merrill and Steiger both treated calcareous rocks with carbonic acid to determine their weathering characteristics and obtained varying degrees of etching, but made little of the possibilities of etching as a tool for the general study of texture, character and distribution of impurities, and in paleontology. Steiger mentions that hydrochloric acid and sulfuric acid were unsatisfactory for his purposes; neither of the two writers describes the use of other kinds of acids. Rittenhouse briefly mentions hydrochloric acid etching as an aid in the study of texture and composition.

A bibliographic review of North American geological literature since 1929 reveals no other specific references to the procedure or its uses. Acid etching tests may have been mentioned or discussed in earlier publications, but these are apparently no longer familiar to many workers. It seems worthwhile, therefore, to describe the method of making the test, its possibilities, and the nature of the results obtained.

The text is accompanied by a series of photographs which show the effects of acid etching on samples from exposures of typical Illinois limestones. The illustrations have been selected to give producers and users of these limestones a better understanding of the nature of some of these rocks and, at the same time, to illustrate some of the more important aspects of acid etching in the field of sedimentary petrography.

The important phenomena shown by the etched samples are briefly discussed in the titles, both from the standpoint of their practical significance and scientific importance. An effort has been made to specify which of the limestones are clastic in origin, in the sense that they were probably deposited as sands. Both the character of the etched specimens and field observations of the deposits from which the specimens came have been considered in this connection. However, no attempt is made to interpret in detail the phenomena shown by the photographs in terms of diagenesis and geologic history of the specimens; these and other related matters are under investigation.

Procedure

An etching test is made as follows: A plane or nearly plane surface is prepared on the specimen of calcareous rock to be studied. The specimen is placed in a flat-bottomed glass or other acid-proof container with the plane surface in such a position that it will approximately parallel the surface of the acid to be added. Acid is added until the specimen is submerged to a depth of 1/2 inch or more. The reaction is allowed to proceed for a brief period. The specimen is then removed from the acid, washed thoroughly but gently, allowed to dry, and suitably examined.

The specimen is placed with its plane surface approximately parallel to the surface of the acid in order to obtain uniform etching conditions. Inclined surfaces of specimens, especially limestone specimens, are apt to become mildly corrugated by localized rising streams of carbon dioxide bubbles which cause more rapid circulation of acid along their paths and thus produce greater local solution. Corrugation of the plane surface is undesirable as it may in some cases be confused with other significant etching phenomena.

A good way to prepare a specimen is to saw or grind it so that it has two essentially parallel flat surfaces and thus may be easily placed with a flat surface parallel to the surface of the acid. If this is not feasible, one surface of a specimen may be ground or sawed flat and the specimen then supported with modeling clay or propped up with pieces of insoluble materials so that the flat surface is level. The flat surface should be finished by grinding with No. 600 carborundum or some other fine abrasive to make it scratch-free; hone may also be used. Samples should be thoroughly scrubbed after grinding in order to eliminate particles of abrasive.

For rough and rapid work, etching of fracture surfaces may prove satisfactory if the rock being studied breaks with relatively smooth and flat surfaces.

The above techniques can be applied to diamond-drill cores but obviously are not applicable in all details to the cuttings from churn-drill or rotary-drill wells. However, the coarser chips in such cuttings can be readily flattened on one or two sides with suitable hones, files, or abrasive paper and can then be etched in the same manner as are larger specimens.

A variety of acids can be used for etching but either hydrochloric or acetic acid gives good results, and as these are common acids they were used in the present study. Relatively dilute solutions should be employed in order to avoid too vigorous effervescence. Ordinarily it is desirable to dissolve about 0.5 mm. of rock from the flat surface. A good etch is generally obtained from a mixture of 23 cc. of C.P. glacial acetic acid in 100 cc. of water with an etching period of 20 minutes, or from 8 cc. of C.P. concentrated hydrochloric acid in 100 cc. of water acting for 5 minutes. Dolomites require a longer reaction time, mild heating of the acid, or both. Experimentation soon shows the best etching time and acid concentration for a particular type of rock or purpose.

After a suitable etching period, the specimens are carefully removed and cautiously washed by immersing them gently several times in water so as to disturb as little as possible the insoluble material adhering to the plane surface of the specimen. Or the acid may be siphoned off and the container gently filled with several changes of water. Specimens which are porous or those which have been in acid for some time benefit from being soaked for a few hours in several changes of water in order to eliminate absorbed salts, such as calcium chloride, which might otherwise appear on the specimens after drying.

Comparison of Hydrochloric and Acetic Acid Etching

Limestone specimens etched in hydrochloric acid ordinarily develop an “acid polish” (fig. 5A), somewhat akin to a polish obtained mechanically, and show only minor differential solution of calcite materials. Projecting above the etched surface are the clay, silt, sand, chert, and other insoluble materials (figs. 3A and
fossils usually
Fossils limestones fine roughly semi-polished dolomite particularly dolomitic etching, after calcite etched grained acetic in acid dissolved and grain and of differences on evident and hydrochloric acids, (fig. 7B, 10A). Coarsely crystalline calcite often appears glassy (fig. 8A). Internal structures of fossils (figs. 5A and 9A) and differences in grain size of calcite particles (fig. 18A) are commonly well shown. Other features of the rock, such as oolite or detrital grains, are brought out clearly (fig. 6A). If weak acid is used, dolomite grains project above the etched surface of the limestone and show relatively minor effects of solution (figs. 20A and 21C).

Acetic acid is less uniform in its etching action on limestone than hydrochloric acid and usually produces a rough surface. The action of the acid appears to be considerably influenced by porosity, incipient fractures, grain contacts, size and relative purity of calcite grains, and other characteristics. After etching, the core of an oolite grain and some of the annular deposits around the core may project more than other annular deposits in the same grain (figs. 6B and 21B). Fossils are also differentially dissolved (figs. 5B, 12B, 21A, and 22B), and large calcite grains exhibit differential etching, possibly along cleavage planes (figs. 7B, 16B, and 22A). However, though acid insoluble materials and dolomite grains in dolomitic limestones are evident after acetic acid etching, they are usually less readily seen than after hydrochloric acid etching because of the common roughness of the surface above which they project (figs. 14, 15, and 20). This is less true of fine-grained rocks than of coarse-grained rocks.

The surfaces of some limestone specimens etched with acetic acid or citric acid are more or less coated with a fine white powder, possibly fine particles of calcite, which masks details. This is particularly evident in the floors of the depressions resulting from the etching of the annular portions of oolite grains. It also develops on some fine-grained limestones. A quick rinse with very dilute hydrochloric acid eliminates the powder and clarifies details.

The etching of dolomite with either hydrochloric or acetic acid produces rough, sandy appearing surfaces. In general, little significant difference has been noted between etched surfaces produced by the two acids, and therefore it is believed desirable to use dilute hydrochloric acid for most work with dolomite because of its more rapid rate of etching. The type of data obtained from etched dolomites is roughly similar to that from limestones though often less spectacular.

**Etching with Other Acids**

The etching of limestones with an aqueous solution of citric acid, having the same amount of available hydrogen ion as the acid-water mixtures previously mentioned, produced results generally similar to those of acetic acid. Differential solution was a little less marked, though in some oolite grains differential solution of the annular material was slightly more pronounced with the citric acid. The effect of the acid on the coarse-grained calcite was similar but less pronounced than that of acetic acid.

Other organic and mineral acids were tried as etching agents for limestone. The organic acids and carbonic acid gave results of about the same character as acetic and citric acids, whereas the mineral acids produced etched surfaces like those of hydrochloric acid. A mixture of acetic and hydrochloric acids yielded an etched surface combining the characteristic effects mentioned above for the acids individually, producing a semi-polished surface showing subdued differential etching. Oxalic acid, sulfuric acid, or other acids that produce relatively insoluble reaction products with calcite or dolomite are usually undesirable for etching.

**Studies of Insoluble Materials**

The undissolved materials on etched surfaces may be carefully removed and studied by the usual petrographic methods. Staining tests, especially the potassium ferricyanide test for dolomite, are effectively applied to etched specimens. In both of these procedures the use of specimens etched by hydrochloric acid is usually preferable because of the greater ease with which the undissolved materials may be distinguished from the groundmass.
Examples of Etching

The accompanying illustrations have been selected to indicate the results of etching different types of limestone with hydrochloric acid and acetic acid, to show the textures of various Illinois limestones, and to depict interesting features, such as lithologic characteristics, distribution and nature of impurities, and fossils. None of these illustrations shows all the various lithologic types of limestone that comprise the formations named.

Comments are appended to most of the illustrations indicating some of a variety of scientific and practical inferences which can be drawn from examination of the etched specimens. For convenience the term "clastic," as used in connection with the illustrations, is arbitrarily applied only to limestones which are believed to have been deposited as sands. The grinding equipment referred to in connection with comments on abrasiveness is fine-grinding machinery such as hammer mills and pulverizers.

In order to provide a comparison between the natural unmagnified appearance of the limestones illustrated and their appearance after etching and magnification, small natural size photographs of 12 samples are shown in figures 1 and 2.

All specimens illustrated are fresh rock with one exception, which is so described. The plane of all photographs is normal or almost normal to the bedding of the specimens. The two etched surfaces of each specimen were prepared by sawing through a hand specimen and using the two sawed surfaces for etching. One was etched by hydrochloric acid and the other by acetic acid. In rare cases only are the photographs of the two surfaces recognizable as counterparts because the width of the cut made by the saw was generally greater than the diameter of the grains comprising the specimens. All photographs were taken by reflected light.

Because of the other objectives of this paper, only general attention is given to the mineralogy of the specimens. No attempt has been made to distinguish between calcite and aragonite; the latter may not be present.

All identifications of fossils named in this paper have been made by Heinz Lowenstam, formerly Geologist with the Areal Geology and Paleontology Division of the Illinois Geological Survey. Photographs were made by Raymond S. Shrode, Assistant Geologist, Industrial Minerals Division of the Survey. The writer expresses his thanks to both of these men for their aid in this study.
ILLUSTRATIONS

Figures 1 to 22
Fig. 1.—Natural size photographs of limestones, enlarged etched views of which are shown on following pages.
A. Ste. Genevieve oolite, Anna, Ill. (fig. 7).
B. St. Louis limestone breccia, Alton, Ill. (fig. 8).
C. St. Louis limestone, Alton, Ill. (fig. 9).
D. Salem limestone, Mill Creek, Ill. (fig. 11).
E. Paint Creek limestone, New Hanover, Ill., weathered surface of slab (fig. 3).
F. Levias oolite, Milltown, Ind. (fig. 5).
Fig. 2.—Natural size photographs of limestones, enlarged etched views of which are shown on following pages.
A. Salem oolite, Valmeyer, Ill. (fig. 13).
B. Salem oolite, Valmeyer, Ill., naturally weathered surface (fig. 14).
C. Kimmswick limestone, Valmeyer, Ill. (fig. 18).
D. Platteville limestone, Dixon, Ill. (fig. 20).
E. Salem limestone, Alton, Ill. (fig. 15).
F. Burlington limestone, Quincy, Ill. (fig. 16).
Paint Creek Limestone near New Hanover, Illinois, × 18

Fig. 3A.—Hydrochloric acid etch. Sand grains and masses of fine-grained silica project above groundmass of mostly clear, relatively coarsely crystalline calcite which photographs black or dark gray; ridges of silica a little below center of right margin.

Fig. 3B.—Acetic acid etch. Sand grains less clearly visible than in A. Local differential deepening of some areas of clear calcite; a few scattered oolite grains present.
Comment.—A clastic limestone, as evidenced by the presence of rounded quartz sand grains. This rock would probably be abrasive to grinding equipment because of the quartz grains and masses of silica; it is relatively impure. It is not likely to be highly weather resistant.
Fig. 4A

LOWER CHESTER RED OOLITE AT SHETLERVILLE, ILLINOIS, × 18

Fig. 4A.—Hydrochloric acid etch. Oolite grains with fine-grained impurities scattered through them; ridges of ferruginous clayey material; scattered quartz grains visible, especially in upper central part.
Fig. 4B.—Acetic acid etch. Differential solution of groundmass leaving oolite grains and pieces of fossils, including crinoid stems, projecting above it; differential solution of core grains of some oolite grains and of centers of crinoid stem fragments.

Comment.—A clastic limestone; moderately pure. The clay partings may adversely affect the weather resistance of the stone.
Levias Oolite, Milltown, Indiana, × 18

Fig. 5A.—Hydrochloric acid etch. Surface of specimen essentially plane, clear calcite matrix; oolite grains, some with several concentric deposits; many elongate pieces of fossils; cross-section of a mollusk and of a bryozoan shown in lower half of photo; a few scattered small masses of fine-grained silica project above smooth surface of specimen.
Fig. 5B.—Acetic acid etch. Specimen deeply etched, giving rough surface; marked solution of white exterior zones of fossil fragments; some fossil fragments almost free; differential etching of bryozoan in lower left corner.

Comment.—A clastic limestone of high purity and essentially free of impurities which might abrade grinding equipment. Its weather resistance is probably good, but in time a surface may result that will have a very subdued resemblance to the acetic acid etched surface.
Fig. 6A

Ste. Genevieve Oolite, Anna, Illinois, × 18

Fig. 6A.—Hydrochloric acid etch. Surface of specimen almost plane; clear calcite matrix; many oolite grains having several annular deposits; fossil fragments surrounded by a single ring of white calcite; small amount of fine-grained quartz; two large quartz grains.
Fig. 6B.—Acetic acid etch. Surface of specimen rough; differential solution of white calcite deposits around fossil fragments and of annular deposits of oolite grains. The latter is well shown near the center of the left half of the specimen.

Comment.—A clastic limestone of good purity and probably good weather resistance. A surface having a subdued similarity to the acetic acid etched surface is likely to result after long weathering.
Ste. Genevieve Oolite, Anna, Illinois, × 18

Fig. 7A.—Hydrochloric acid etch. Surface of specimen almost plane; clear calcite matrix; oolite grains, some showing several annular deposits; coarse fossil fragments with single exterior ring of white calcite; several projecting small masses of fine-grained silica with one large mass in the upper righthand corner of specimen; numerous small dolomite rhombs, especially near center top margin.
Fig. 7B.—Acetic acid etch. Surface of specimen rough; differential etching of white calcite deposits around fossil fragments and of annular deposits around centers of oolite grains; differential solution of calcite composing fossil fragments along possible cleavage planes.

Comment.—A clastic limestone probably having good weather resistance. Long exposure to the weather is apt to produce a surface having a much subdued resemblance to the acetic acid etched specimen.
Fig. 8A

St. Louis Limestone Breccia near Alton, Illinois, × 12

Fig. 8A.—Hydrochloric acid etch. Surface of specimen almost plane; dark areas are clear calcite; angular fragments of limestone in a clear calcite cement; small amount of fine-grained quartz scattered over surface.
Fig. 8B.—Acetic acid etch. Differential solution of calcite cement; deepening of incipient joints or contacts between limestone fragments; impurities not as well shown as in A.

Comment.—A relatively pure limestone of doubtful weather resistance because of possible failure along calcite veins.
Fig. 9A

**St. Louis Limestone, Alton, Illinois, × 12**

*Fig. 9A.*—Hydrochloric acid etch. Surface of specimen essentially plane; relatively large fossils and fossil fragments in groundmass of ill-defined texture; fossil in lower part of picture is probably a foraminifer; the dark wavy area in the upper half of the specimen is transparent calcite of a brachiopod shell. Small deposits of silica, probably chalcedonic, project above the groundmass in the upper third of the specimen.
Fig. 9B.—Acetic acid etch. Surface of specimen rough; detrital material in limestone well shown by differential solution; large calcite masses shown which are not evident in A. A fossil, probably a foraminifer, showing differential etching, lies just below center of specimen.

Comment.—A limestone possibly formed by the accumulation of “lime” mud in which the remains of incidental fossils were included. The rock is probably of high purity and good weather resistance.
Fig. 10A

Salem Limestone, Columbia, Illinois, X 18

Fig. 10A.—Hydrochloric acid etch. Surface of specimen almost plane; a limestone composed of fragments of fossils and other materials in a clear calcite matrix; foraminifera visible just below center of left margin of specimen; masses of white fine-grained silica project above surface.
Fig. 10B.—Acetic acid etch. Surface of specimen rough; probable clastic character of rock and texture well shown; differential solution of matrix; impurities not as well shown as in A but several large masses of silica present.

Comment.—Probably a clastic limestone, of moderate purity. It is apt to be mildly abrasive to grinding equipment because of the silica content.
Salem Limestone, Mill Creek, Illinois, × 12

Fig. 11A.—Hydrochloric acid etch. Surface essentially plane; no impurities evident; white material is fossil fragments, especially of bryozoans; matrix clear calcite.

Fig. 11B.—Acetic acid etch. Surface of specimen rough; notable differential
solution of fossil detritus leaving calcite groundmass projecting; a differentially etched coral in lower right corner.

Comment.—A limestone of high purity and of clastic origin. The deep etching of the bryozoan fossil material by acetic acid suggests that the stone would have a tendency to develop a rough granular surface on long continued exposure to the weather.
Salem Limestone, Ste. Genevieve, Missouri, $\times 12$

Fig. 12A.—Hydrochloric acid etch. Surface essentially plane; a clastic rock comprised of oolite grains and fossil detritus; dark areas are clear calcite; large fragment of crinoid stem just below and a little to right of center of specimen; a few small grains and masses of silica project above groundmass.
**Fig. 12B.**—Acetic acid etch. Surface rough; notable differential etching; clastic character of limestone well shown; fossil fragments project notably above groundmass; crinoid stem fragments in lower half of specimen show differential solution; in the upper righthand corner is a spine, possibly of an echinoid; presence of impurities not well shown.

*Comment.*—A clastic limestone of high purity and probably good weather resistance.
Salem Limestone, Valmeyer, Illinois, × 18

*Fig. 13A.*—Hydrochloric acid etch. Surface of specimen essentially plane. Numerous oolite grains; foraminifera evident, especially in lower right part of specimen; clear calcite groundmass; scattered small grains of silica.
**Fig. 13B.**—Acetic acid etch. Surface rough; differential solution of annular deposits of oolite grains; large masses of crystalline calcite; impurities not well shown. *Comment.*—Same as for figure 12.
**Salem Limestone, Valmeyer, Illinois, \( \times 18 \)**

**Weathered Rock**

*Fig. 14A.*—Hydrochloric acid etch. Surface moderately rough due to projecting masses of silica and possibly of clay in the lower half of the specimen; numerous oolite grains; silica replacing crinoid stem shown in upper right of specimen.
Fig. 14B—Acetic acid etch. Rough surface; differential etching of annular deposits of oolite grains and of calcite groundmass; enlargement of fracture indicated by branching black linear area extending from top to bottom of specimen; distribution of impurities generally not well shown.

Comment.—A clastic limestone of moderate purity. The sample will probably be abrasive to grinding equipment.
Salem Limestone, Alton, Illinois, × 18

Fig. 15A.—Hydrochloric acid etch. Essentially plane surface but with numerous masses and grains of silica and some clay projecting above groundmass; large mass of fine-grained silica near lower left corner; rock composed largely of fossil debris, indistinctly shown.
Fig. 15B.—Acetic acid etch. Surface rough; differential etching of groundmass with fossil detritus clearly projecting from surface of specimen; clastic character of rock well shown; impurities not readily evident.

Comment.—An impure, clastic limestone, probably abrasive to grinding equipment. Resistance to weathering possibly fair to good.
Burlington Limestone, Quincy, Illinois, X 12

Fig. 16A.—Hydrochloric acid etch. Essentially plane surface; pieces of crinoid stems numerous; large masses of crystalline calcite; matrix clear calcite; scattered white silica grains and one relatively large mass of fine-grained silica at upper right.
Fig. 16B.—Acetic acid etch. Differential solution of matrix with large grains of projecting calcite; differential etching of large grains brings out probable cleavage.

Comment.—A clastic limestone of high purity. The acetic acid etch reveals that many of the coarse particles are single calcite crystals.
GIRARDEAU LIMESTONE, THEBES, ILLINOIS. × 18

Fig. 17A.—Hydrochloric acid etch. Surface rough due to the presence of a large amount of fine-grained silica; some differential solution of fine-grained calcite groundmass.

Fig. 17B.—Acetic acid etch. Solution of calcitic fossils and masses of calcite shown by black areas representing holes in the etched surface. Enlarged minute frac-
ture or incipient crack extending left to right in upper half of specimen.

Comment.—An impure siliceous limestone which may well have been deposited as a gritty lime mud. The rock is likely to be abrasive to grinding equipment. It will probably develop a light gray coating of silica when exposed to the weather, but is apt to have good weather resistance, though obscured incipient fractures may produce unexpected failure in some cases.
Kimmswick Limestone, Valmeyer, Illinois, × 12

Fig. 18A.—Hydrochloric acid etch. Essentially plane surface; coarsely crystalline calcite abundant; bryozoan material at right center of specimen.
Fig. 18B.—Acetic acid etch. Differential solution of fossil material; much of the central etched-out area was probably originally bryozoa.

Comment.—A crystalline limestone of high purity.
Kimmswick Limestone, Thebes, Illinois, X 18

Fig. 19A.—Hydrochloric acid etch. Surface essentially smooth; medium crystalline limestone with two stylolites, one in upper righthand corner and one near center of specimen, with small amount of clay along them.
Fig. 19B.—Acetic acid etch. Rough surface; differential solution of calcite grains brings out grain size and texture; etched stylolite in lower left portion of specimen.

Comment.—A crystalline limestone of high purity.
Platteville Limestone, Dixon, Illinois, × 12

Fig. 20A.—Hydrochloric acid etch. A fine-grained dolomitic limestone containing fossils; gastropod at the right center of the photograph consists of clear calcite, which photographs black, and is filled with finer grained calcite; masses of dolomite in lower right and upper left corners with dolomite grains scattered throughout most of specimen.
Fig. 20B.—Acetic acid etch. Areas of dolomite in lower left and upper right corner of specimen; fossil of clear calcite, photographing black; enlarged fracture shown in lower part; scattered dolomite grains not as well shown as in A.

Comment.—A dolomitic limestone of high purity; may have been deposited as a "lime" mud with incidental fossils. Development of dolomite appears to be secondary.
Fig. 21
LIMESTONES AND DOLOMITES

Miscellaneous Specimens

Fig. 21A.—Acetic acid etch. Differential etching of bryozoa in Kimmswick limestone from Valmeyer, Illinois. Large mass of fine-grained silica at left end of bryozoa; rest is calcite. × 16.

Fig. 21B.—Acetic acid etch. Differential etching of oolite grain with core grain projecting above annular deposits and differential solution of annular deposits. Ste. Genevieve limestone, Anna, Illinois. × 35.

Fig. 21C.—Acetic acid etch. Differential etching of dolomitic limestone with dolomite grains projecting above groundmass. Platteville limestone, Dixon, Illinois. × 35.
Fig. 22
Fig. 22A.—Acetic acid etch. Etch pattern produced on polished surface of cleavage block of white calcite. The striae-like interrupted grooves extending diagonally from left to right are not scratches which were present on the unetched specimen but were produced by the etching. × 16.

Fig. 22B.—Acetic acid etch. Differential etching of crinoid arm plates. Ste. Genevieve limestone, Anna, Illinois. × 35. A similar spongy structure also commonly results from acetic acid etching of other parts of crinoids.