

CLAY POLYMERIZATION IN CARBONATE ROCKS: A SILICIFICATION REACTION DEFINED

by

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ABSTRACT

A carbonate rock silicification reaction has been defined and shown to be dependent on the presence of clay in the host rock. Introduction of silica in soluble form(s) serves to polymerize the clay fraction, forming a continuous three-dimensional network. This siliceous network (polymer) can be separated from the rock by leaching away the carbonate minerals. Laboratory silicification of argillaceous carbonate rocks under controlled conditions has served to define critical variables.

Early studies were limited to argillaceous carbonate rocks from the Devonian Cedar Valley formation in eastern Iowa. Similar results have been obtained with carbonate rocks from the Devonian Chaffee formation in south-central Colorado. Some of the rocks in the latter formation have been silicified in nature, and yield siliceous polymers on acid leaching identical to those formed by silicification in the laboratory.

The reaction defined is suggested to be common in natural diagenesis of argillaceous rocks, clay-rich sedimentary material, and soils.

In the case of argillaceous carbonates this reaction affects *physical* properties of the rock which control processes involved in petroleum migration, ore-metal transfer, rock leaching and all diagenetic reactions that involve solution transfer.

INTRODUCTION

Studies of the chemical stability of certain carbonate rocks as coarse aggregate in concrete have served to demonstrate and define a silicification reaction which involves the clay fraction of these rocks (Bisque 1959; Bisque and Lemish 1958, 1959, 1960; Lemish, Rush and Hiltrop, 1958; and Hiltrop and Lemish, 1960). The silicification is rapid enough at slightly elevated temperatures to be effected in the laboratory. This has permitted objective evaluation of the variables involved. Hiltrop and Lemish (1959) corroborated the results of the forementioned reports by a unique experiment which will be described.

The reports cited above were written in light of the engineering implications of the studies; *i.e.* the chemical stability of concrete containing these carbonate rocks as coarse aggregate was the main consideration.

The rocks involved were argillaceous, dolomitic carbonates from the Devonian Cedar Valley formation in eastern Iowa.

This contribution will review briefly the pertinent observations and conclusions of these previous studies, describe similar results obtained with carbonate rocks from another area, and discuss the proposed petrologic and geologic significance of the reaction. Thus far there have been no reports of this reaction having been effected artificially in carbonates from other areas. The rather distinct petrography of these Iowa Devonian carbonates (Lemish, Rush and Hiltrop, 1958) led to speculation that the reaction was peculiar to rocks from the Cedar Valley formation. Recent study has shown that argillaceous carbonates from the Devonian Chaffee formation exposed in south-central Colorado are subject to this same type of silicification. No significance is attributed to the fact that the rocks in both cases are Devonian in age. Some of the latter are petrographically distinct from the Iowa carbonates and others are strikingly similar (Plate 1). Discussion of the Colorado rocks will follow summarization of the earlier studies.

OBSERVATIONS AND CONCLUSIONS OF THE IOWA STUDIES SUMMARIZED

When used as coarse aggregate in concrete the rocks in question were observed to be host to chemical activity which resulted in visible dark shells in the periphery of the carbonate rock aggregate particles. Chemical, petrographic, X-ray and pore volume studies furnished data which substantiate the following facts regarding the growth of these reaction shells.

(1) Silica is introduced with little or no concomitant loss of chemical constituents from the host rock.

The reaction shells were observed to be more resistant to acid (HCl) etching than the unaffected host rock. Chemical analysis of similar rock fragments, before and after equilibration with solutions of silica in the laboratory, showed a definite and appreciable increase in silica content with little change in other rock constituents. X-ray and petrographic analyses indicated no new mineral phase in the rocks which had consumed silica.

Samples of host rock and corresponding silicified shell-zone material were carefully separated from concrete samples and analyzed chemically to verify further the above observations.

The mass of the host was shown to increase as the silicification progresses. Weight changes of both argillaceous and nonargillaceous rocks were followed during equilibration with a solution of silica. The argillaceous rocks gained weight while the nonargillaceous did not. The latter actually lost weight owing to leaching of minor amounts of soluble components ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, etc.) by the solution.

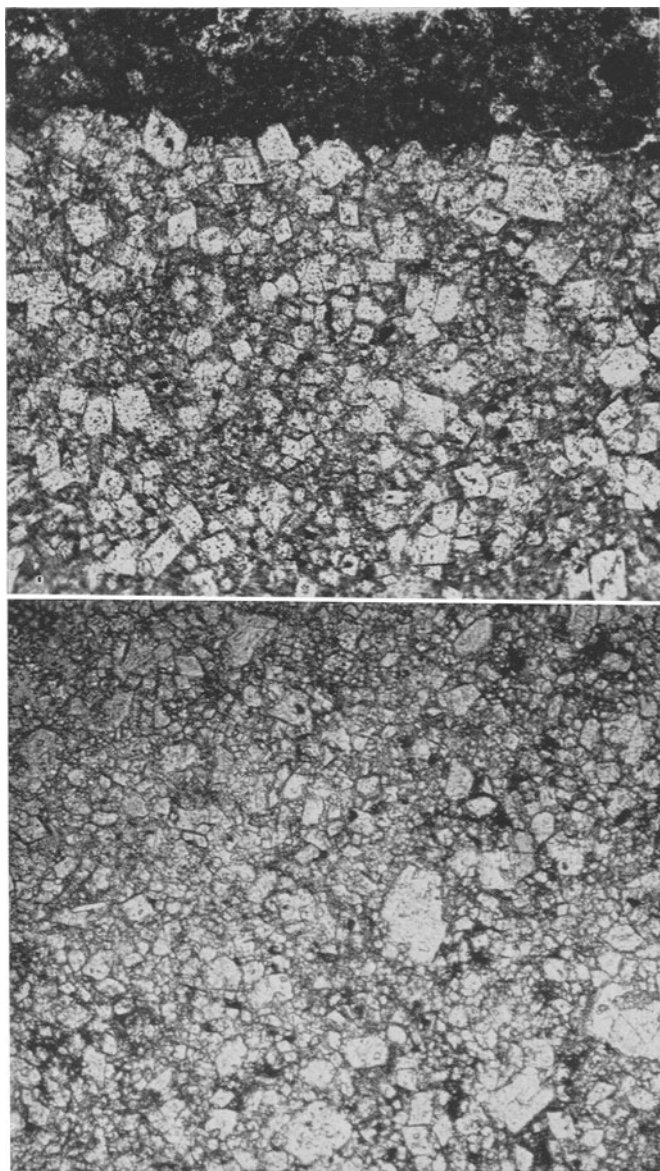


PLATE 1.—Thin-section. (a) A typical argillaceous dolostone from the Devonian Cedar Valley formation. The dark portion at the top of the picture is not part of the rock texture. X 100. (b) An argillaceous dolostone from the Chaffee formation in Colorado which yields a siliceous polymer similar to those formed in the type of rock with the texture shown in (a). X 150.

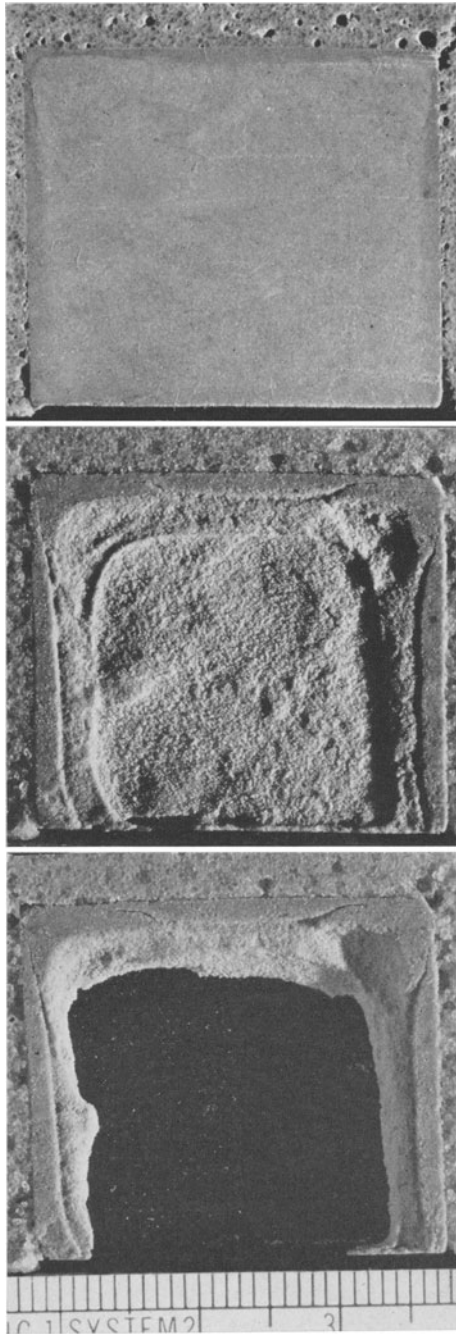


PLATE 2.—Successive acid leaching of a wafer cut from a machined block of argillaceous rock which has been silicified in the laboratory. The top photograph demonstrates that penetration of the silicification may not be visible. The rock is imbedded in a concrete matrix. Note the lesser degree of silicification which has taken place at the carbonate rock-aqueous solution interface (middle photo).

(2) The pore volume (*i.e.* "total effective porosity") as measured with a mercury capillary injection apparatus (Bisque and Lemish, 1958, p. 39; Bisque, 1959, p. 28) is reduced as the silicification progresses.

Complementary to observation (1) above, one would expect a decrease in the pore volume of the host rock. This decrease was demonstrated in two ways; (a) pore volume measurements were made on host rock and corresponding shell-zone samples taken from the concrete samples; (b) pore volume measurements were made on carbonate rock fragments before and after controlled silicification in the laboratory. Each of these approaches showed a decrease in total pore volume with silicification. The decrease for the rocks studied was of the order of 60 percent, the average being a decrease from approximately 6 percent (absolute) to 2 percent or less.

(3) The introduced silica serves to cause the formation of a continuous three-dimensional framework throughout the host rock. The carbonate minerals may often be leached away, separating this siliceous framework with little mechanical damage.

After silicification has been effected, the carbonate minerals may be leached away with hydrochloric acid, leaving a delicate, pumice-like structure. If the silicification process is halted before the entire particle is affected, its progress can be ascertained by acid leaching of sections cut perpendicular to the surface being attacked (Plate 2).

(4) Only clay-bearing carbonate rocks are subject to this type of silicification.

In all phases of the investigations being reviewed, nonargillaceous rocks were treated similarly for comparisons. These were not silicified, nor were all of the argillaceous rocks which were tested.

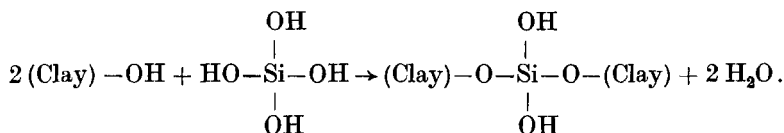
(5) The same type of silicification can be effected readily by subjecting these rocks to a vaporous mixture of volatile silane derivatives, CH_3SiCl_3 and $(\text{CH}_3)_2\text{SiCl}_2$ (Hiltrop and Lemish, 1959).

By producing the same silicification product by an entirely different reaction and in a different medium, this experiment served to substantiate conclusions arrived at by consideration of points (1) to (4). The silane-derivative reaction demonstrates that silicon alone can effect the formation of the polymer; aluminum or other elements are not required. In addition, it indicates that monomeric silicon-containing molecules are sufficient. This fact is pertinent because when dealing with aqueous solutions of silica one cannot be certain that longer chain-polymers (oxyanions) of silicon (*i.e.* $\text{Si}_3\text{O}_9^{-8}$, etc.) are not solely responsible for effecting the silicification.

The presence of the hydrophobic methyl groups introduces a waterproofing which of course does not occur in silicification in aqueous solutions.

The observations summarized above led to the postulation that the introduced silica is stabilized in a continuous three-dimensional polymer which includes the clay fraction of the rock. It is visualized as a simple conden-

sation polymerization in which linking bonds are formed by the "splitting off" of a water molecule between a hydroxyl group on the surface (or edge) of a clay particle and similar groups on a silicon oxyanion (H_4SiO_4 , H_3SiO_4^- , $(\text{Si}_n\text{O}_{3n})^{-2n+1}$, etc.). In the case of the silane-derivative reaction, the $-\text{OH}$ radicals are formed when $-\text{Cl}$ radical is hydrolyzed by moisture in the vapor. A single step in the polymerization might be diagrammed as follows:



Several soluble ions may be involved in breaching the gap between siliceous host-rock constituents. Continuation of this condensation polymerization in three dimensions readily accounts for each of the experimental observations cited in the preceding review. Bisque and Lemish (1959) demonstrated that the weight of the pumicelike structure which remains after removal of carbonate minerals is at least several times greater than the weight of the silicon which was introduced to cause its formation. Exact weight relationships are difficult to determine in this way because of the fragile nature of the siliceous network formed.

The Iowa carbonates studied were dolomitic (Bisque and Lemish, 1959a). The texture of the majority of them was intermediate to that of the "sucrose dolomite" and "interlocking dolomite" as described and figured by Murray (1960, Figs. 8 and 1). The dolomite rhombs are comparatively free of noncarbonate impurities as compared to the matrix. Because of this, silicification affects the matrix and not the well defined rhombs. The skeletal network resulting from removal of carbonate minerals from a silicified rock therefore contains perfect casts of the dolomite rhombs (Plate 3). This has been observed in the leached siliceous framework of carbonates from Colorado as well.

DISCUSSION

The word "clay" in this discussion and the preceding text refers to the finely divided noncarbonate fraction, excluding, of course, pyrite and other nonsiliceous constituents. It is meant to include crystalline clay minerals and all aluminosiliceous material ranging from poorly crystalline to amorphous. Bisque (1959) presented data which indicate that much of the clay-size material in many of the Iowa carbonates is amorphous or pseudo-amorphous. The fine material was separated from powdered carbonate rock samples by flotation, concentrated by centrifugation or 24 hr of gravity settling, and then allowed to settle from a slurry onto a glass slide. X-ray examination demonstrated that the only crystalline material present in this fraction

was an illitic clay. Chemical analyses of this same fraction gave silicon: aluminum ratios in the order of 2:1. Since a crystalline illite such as was detected by X-ray would not tolerate aluminum substitution much beyond 6:1 (Grim, 1953, p. 67) it was concluded that a significant amount of aluminum-rich amorphous material was separated with the illitic clay. Because definitive X-ray diffraction patterns of the crystalline material were readily obtained (Bisque and Lemish, 1958, p. 34), no attempt was made to separate the noncrystalline material.

The fact that the casts of dolomite rhombs which remain in the siliceous skeleton after acid leaching are exceptionally well defined (Plate 3) is interesting. It demonstrates that much of the noncarbonate material is concentrated at the dolomite crystal faces, thereby facilitating the polymerization which results in the rigid "walls" of the casts. This situation may be interpreted to indicate that the noncarbonate constituents were expelled as material was reworked and subsequently organized to form the secondary dolomite. If a similar process were to continue as the calcitic matrix developed larger crystals, it would not be unreasonable to assume the possibility of a rather complete expulsion of siliceous and aluminous constituents from the carbonate phases. This would result in a rock in which most of the siliceous constituents were concentrated at grain boundaries (pore walls of the rock). This situation would facilitate transfer of the silica and alumina by the action of solutions. Subsequent aggregation of this dispersed phase at sites of greater chemical stability would take place. Since pH conditions that would cause precipitation of silica (and possibly alumina) are the same as those that would dissolve calcite or dolomite or both (Mason, 1958, p. 160), replacement of preferred volumes in carbonate rocks would be likely. Such replacement might well be initiated and facilitated in clay-rich volumes in the rock by a mechanism similar to the one being described in this discussion. The ultimate result would be the formation of a separate phase commonly observed in carbonate rocks: chert.

A suitable balance of pH conditions and solution transfer at the site of aggregation (precipitation) would permit preservation of rock texture and structure in the chert phase. This postulation inherently includes the not uncommon supposition that the silica required for epigenetic chert formation is derived from materials syngenetic with the host rock (Biggs, 1957).

The carbonate rock from which the siliceous material is derived may or may not experience a change in porosity. This would depend on (a) the total amount removed per unit volume and (b) the extent and trend of diagenesis which has preceded and/or accompanied removal of noncarbonate material. If a substantial network of dolomite rhombs is present to buttress the rock against diagenetic compaction (Weyl, 1960) a pronounced increase in porosity may result. If compaction keeps pace with or follows the loss of noncarbonate constituents, the end product may be a pure, dense rock.

Evidence to date indicates that argillaceous carbonates having textures similar to those shown in Plate 1 are most likely to form the continuous siliceous polymer. This is probably because the formation of dolomite has concentrated much of the siliceous material on crystal faces, thereby facilitating the polymerization and formation of a rigid three-dimensional framework. The siliceous material, then, is not randomly scattered throughout the rock but concentrated and possibly oriented on the surface of connecting "planes" and "channels." This is the same situation referred to in preceding discussion to explain the well-defined casts of dolomite rhombs in the polymer. Argillaceous carbonates with other textures may contain appreciable amounts of clay material (4 percent or more), "consume" silica from solution, and yet fail to yield a substantial polymer on acid leaching. Bisque (1959) referred to this same textural characteristic to explain the effective gravity separation of clay minerals which could be made by grinding the carbonates to a fine mesh and floating off the clay material. Grinding would fracture the rocks preferentially along the surfaces on which clay material was concentrated, facilitating mechanical abrasion and separation by a dispersing solution.

In a study of the separation of clay minerals from carbonate rocks, Ostrom (1961) concluded that physical methods of separation are likely to be of limited use and applicable only for those rocks in which the clay minerals are properly situated with respect to the carbonate minerals.

SILICIFICATION OF COLORADO CARBONATES

Several of the argillaceous carbonates from the Devonian Chaffee formation in south-central Colorado apparently have undergone silicification of the type being described at some stage of diagenesis. The crystalline clay fraction gave X-ray diffraction patterns which were essentially those of muscovite. Broadening of several lines indicates a trend toward illitic character. When samples of these rocks are carefully leached of carbonate minerals, the clay material remains in a fragile, three-dimensional network. Some of the finer siliceous material, however, is mechanically carried into suspension by agitation of the reaction (*i.e.* the evolution of carbon dioxide). A colloidal suspension results and the fragile skeleton often floats to the top of the solution because of bubble entrapment. The above behavior is in contrast to that of the *same* rock if it is further silicified in the laboratory before being treated with acid. In the latter case, a colloidal suspension does not form because of the stabilization of all colloidal material in the three-dimensional polymer. It is also more difficult to etch all the carbonate minerals from the fragment after this "second stage" silicification. This is because the polymerized material in the periphery of the particle forms a much more effective bubble trap and mechanically blocks solution transfer, thereby preventing further solution of carbonates in the interior (Plate 4).

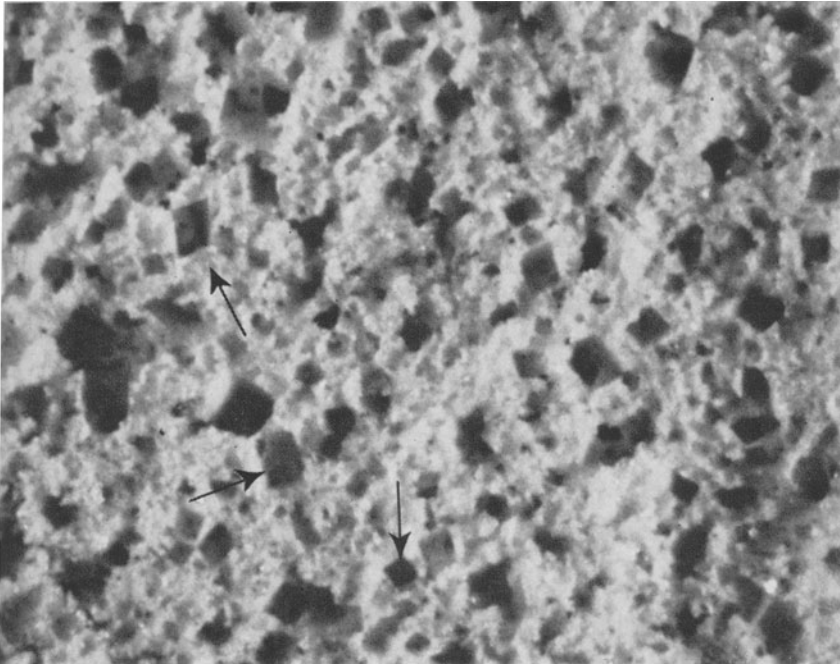


PLATE 3.—Photomicrograph (X 60) of an acid-leached siliceous polymer showing perfect "casts" of dolomite rhombs. This polymer was formed in the rock which is shown in thin-section in Plate 1*a*.

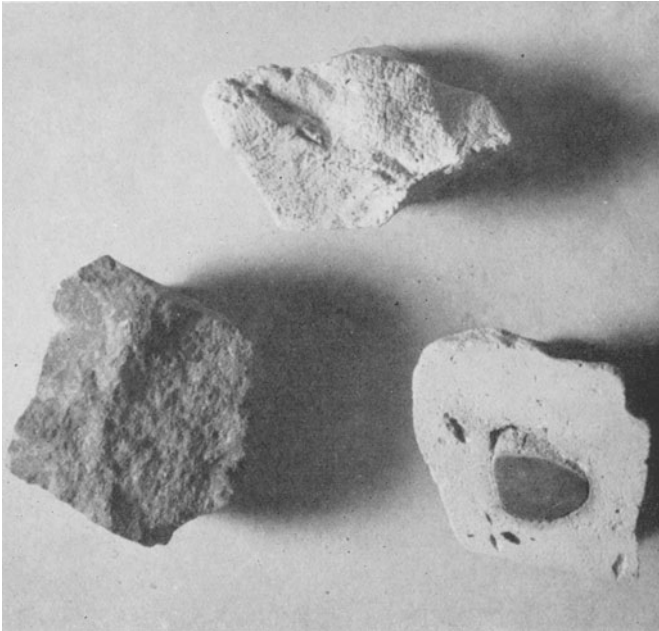


PLATE 4.—Left—fragment of an argillaceous dolostone from the Devonian Chaffee formation. Upper center—a similar fragment which has been silicified in the laboratory and leached of carbonate minerals. Right—a similar fragment which has been sectioned to show an interior core of unleached host rock. Fragments are approximately 2 in. in diameter.

In natural situations, this type of silicification may result in either a reduction or an increase in total porosity, depending on the nature and degree of other accompanying diagenetic changes. If leaching of carbonates is negligible, the addition of silica and formation of the polymer would appreciably decrease porosity. Bisque (1959, p. 28) experimentally demonstrated a decrease of 60 percent. The total effective porosity of the rocks studied decreased from approximately 6 percent to 2 percent in a period of 2 weeks using silica solutions in the 100 ppm range.

On the other hand, it is feasible that silicification might progress to a degree such that the continuity of the polymer and its resultant contribution to the compressive strength of the rock could reduce the amount of compaction that normally would occur when carbonate minerals are removed by leaching. In this case leaching would result in a very porous rock.

The reaction is also very probably involved in cementation of argillaceous shales and certain clay-rich soil materials. If clay material is present in appreciable amounts and well distributed, subsequent addition of silica would serve to form a strength-contributing network. The structure would be less easily recognized in such materials because the bulk of the host material would not be as readily separated from the three-dimensional polymer as in the case of carbonate rocks. Preferred orientation of clay particles in an unconsolidated material, and subsequent polymerization of these particles by silica from percolating solutions, would develop pronounced platy or fissile structure.

LABORATORY SILICIFICATION AND STUDY OF CARBONATES

In the laboratory silicification has been effected in solutions of pH 9–12 and silica concentrations as low as 50 ppm. These solutions were prepared by dissolving crystalline sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) in water and were maintained at 40–50 °C during silicification. Complete polymerization of the clay material in 20-mesh fragments requires from 1 to 3 days, depending on the amount and nature of the clay material.

Changes in silica content of the reacting solution cannot be determined gravimetrically; the low concentrations and small changes involved must be determined spectrophotometrically. The method of Carlson and Banks (1952) which involves the formation of molybdisilicic acid and subsequent reduction to a heteropoly-blue complex ion was used in the investigations cited. Polyethylene containers should be used in conjunction with studies employing the spectrophotometric method of determination to prevent introduction of silica from glass. These measures are not necessary, however, merely to establish whether or not a given carbonate rock is susceptible to silicification. This may be determined by equilibrating a portion of the rock sample with a 0:05 molar solution of sodium metasilicate at slightly elevated

temperature for 3 days. By placing these treated fragments in 3 N hydrochloric acid (1 HCl:3H₂O) and comparing their behavior with untreated fragments placed in a similar solution, one can readily ascertain changes due to silicification.

Carbonate rock samples were chemically analyzed with the use of ethylenediaminetetra-acetic acid (EDTA). This reagent may be used to determine calcium, magnesium, iron and aluminum in most carbonate rocks (Bisque, 1961). Tennant and Berger (1957) present an X-ray method for the determination of calcite/dolomite (mineral) ratios. For this same purpose, Hiltrop and Lemish (1960) developed a method which combines chemical and X-ray techniques. The latter paper discusses the problem of accurate mineral ratio determination and offers suggestions for further refinement.

CONCLUSIONS

Elucidation of the mechanism of this silicification reaction demonstrates that clay material, although a minor constituent, may have a critical influence on the diagenesis of a carbonate rock.

In the case cited the clay fraction of these rocks renders them susceptible to a chemical reaction which affects the porosity and permeability of the rock, thereby affecting physical properties which control processes such as petroleum migration, ore-metal transfer, and rock leaching.

Awareness of the contribution of minor mineral constituents to the chemical reactivity and related *physical* changes of a carbonate rock will aid in interpretation of diagenesis.

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