PERIODS OF FOSSIL FILLING AND REPLACEMENT AS INDICATORS OF CLIMATE

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Embedded within the gray Permian limestones of the Finlay Mountains, trans-Pecos, Texas, are abundant remains of fusulinids, bryozoans, and brachiopods. Most of the fossil tests which are exposed on weathered surfaces are partially, or wholly, replaced by a form of impure silica. The fusulinids especially are characterized by such replacements and stand out in sharp relief above the weathered surfaces of the limestones that contain them.

Besides the one period of silicification exhibited by these fossils, two periods of calcite filling are evidenced also. Chronologically these periods may be listed as follows (Fig. 1):

Period 1.—Calcite filled the voids of the fusulinid shells.

Period 2.—Silica replaced, either partially or completely, the calcareous shell material itself.

Period 3.—Veinlets of calcite and caliche filled fissures that cut the silicified fusulinid tests.

These three distinct periods deserve an explanation. As suggested in this paper, local climatic changes might be the explanation desired.

Description of Area and Fossils

The Finlay Mountains lie on the southwestern margin of the Diablo Plateau, 35 miles northwest of Sierra Blanca, Texas. Permian rocks crop out in the central portion of the mountains and are surrounded on all sides by cuesta-forming Cretaceous beds. Here the climate is typically arid, the average rainfall being 9 inches per year and the average yearly temperature 80° F. In the summer temperatures customarily rise to 100° F, or more, during the day and fall as low as 40° F at night. Vegetation consists of scattered clumps of catclaw, yucca, ocotillo, greasewood, and cacti.

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Ephemeral streams, which flow sporadically in narrow arroyos, drain the region in a southwesterly direction to the Rio Grande. After extremely heavy rains, sheetfloods develop and sweep across a pediment surface that stretches westward from the mountains. The dry, barren, buff and red alluvial wastes of the Hueco Bolson on the west add to the picture of heat and desolation presented by the region.

Fossil replacement and fillings.—Abundant remains of fusulinids, bryozoans, and brachiopods occur in the dark gray arenaceous limestones of the Permian rocks exposed. On the weathered surfaces of these limestones, standing out in bold relief, are the wholly and the partially silicified specimens of fusulinids and bryozoans (Fig. 2). The silicified specimens continue to be present in a thin zone (1 to 2 inches deep) below the weathered surface. However, below this zone in the fresh rock, these fossils tend to be unsilicified and consist entirely of CaCO₃. The hypothesis to be presented is based largely upon the replacement characteristics of fusulinid tests.

In general the original shelly portion of the fusulinids is the only part of the fossils that is silicified. $CaCO_3$ occupies most of the original voids, or chambers, of the shells, although in many specimens the chambers also are silicified. Silicification apparently initiated in the centers of the shells and progressed outward. Hence, shells that are partially silicified are replaced only in their interiors, the outer whorls still being CaCO₃. Erosion has removed these outer whorls, leaving the inner silicified tests protruding above the surface of the containing limestone (Fig. 3).

Replacement of the carbonate of the original shells by silica is most remarkable and in many cases results in perfect preservation of both exterior and interior features of the fossils. A thin sagittal section of one of the silicified fusulinids displays very clearly the microscopic alveolar structure of the inner layer *(keriotheca)* of the fusulinid shell wall.

Numerous small fissures transect the fossil remains regardless of whether or not they are silicified. These fissures are not confined to the fossils alone, however, but continue into the containing limestone (Fig. 4). At the present time CaCO₃, either in the form of calcite or caliche, fills these fissures, forming light gray veinlets which give the dark limestone a streaked appearance.

Other occurrences of fossils associated with silica.-The Hinde reports association of fossils with silica is common. the occurrence of casts of gastropods in the cherts of southern Australia' and casts of brachiopods and crinoid stems in the Carboniferous cherts of Ireland².

According to Barton³ the Mississippian cherts of the Saint Louis (Missouri) region contain many calcareous tests.

Woodward' notes the abundance of silicified fossils in the Paleozoic cherts of west-central Virginia. Van Tuyl⁶ and Howell[®] also have recorded such occurrences.

The writer does not maintain that the hypothesis which follows can be applied to all such fossil-silica associations. Especially does the occurrence of calcareous tests in chert^{*} require some other explanation. However, it would seem that many silicified fossils reported in the literature may have originated under the conditions set forth in the hypothesis.

Relation of Periods of Filling and Replacement to Climate

Formation of calcium carbonate veinlets.-Blanketing the surfaces of many localities in the arid and semi-arid southwestern United States are dirty white nodular deposits of porous, earthy calcium carbonate. These deposits

¹Hinde, G. J.: "Note on Specimens of Cherty Siliceous Rocks from South Australia," Geological Magazine, vol. VIII, decade III, 1891, pp. 115-116.

²Hinde, G. J.: "On the Organic Origin of the Chert in the Carboniferous Limestone Series in Ireland, and Its Similarity to that in the Corresponding Strata in North Wales and Yorkshire," Geological Magazine, vol. IV, decade III, 1887, pp. 435-446.

³Barton, D. C.: "Notes on the Mississippian Chert of the St. Louis Area," Journal of Geology, vol. 26, 1918, p. 364.

Woodward, H. P.: "Paleozoic Cherts of West-Central Virginia," Journal of Geology, vol. 39, 1931, pp. 277-287. ⁵Van Tuyl, F. M.: "The Origin of Chert," American Journal of Science, vol.

^{195, 1918,} p. 452.

⁶Howell, J. V.: "Silicified Shell Fragments as an Indication of Unconformity," American Association of Petroleum Geologists Bulletin, vol. 15, 1931, pp. 1103-1104. ⁷Barton, D. C., loc. cit.

are commonly termed "caliche." One of the best known occurrences of caliche is in the Upper Reynosa formation of southwestern Texas. Price^s, in his excellent paper on this formation, describes the caliche of the Upper Reynosa in detail and presents a convincing argument for its origin. Though caliche often occurs as a nodular bedded deposit, it more frequently acts as cementing material in the Tertiary-Quarternary alluvial deposits of southwestern Texas and tends to be deposited as veinlets in the joints and fissures of the country rock.

The most popular and logical explanation for the formation of caliche is that advanced by Weeks[®] and Price¹⁰. During periods of sporadic precipitation in arid and semiarid regions, meteoric waters unite with the limited CO₂ in the air and soil to form carbonic acid (H₂CO₃). Upon striking CaCo₅, or CaCO₅-MgCO₅, the carbonic acid solution dissolves the carbonate, forming a bicarbonate solution. Following a rain (period of solution), heat causes exaporation of water near the ground surface. This phenomenon in turn causes the deeper waters, which carry the bicarbonate solution, to be drawn upward by diffusion, and upon approaching the heated ground surface the solution loses CO₂, which results in the deposition of CaCO₃. In addition to deposition by upward circulating waters, some CaCO₃ may also be deposited by those circulating downward. In the latter instance any process (e.g. agitation or rise in temperature) which tends to remove CO₂ from the water will cause the deposition of $CaCO_{5}$.

In a limestone region of arid climate, optimum conditions for the formation of secondary $CaCO_s$ should exist. The Finlay Mountain locality is just such a region at present. Thus the origin of the veinlets of $CaCO_s$ which slice through the Permian limestones and fossils of this area can be attributed to the process outlined in the preceding paragraph.

[&]quot;Price, W. A.: "Reynosa Problems of South Texas, and the Origin of Caliche," American Association of Petroleum Geologists Bulletin, vol. 17, 1933, pp. 488-522.

⁸Weeks, A. W.: "Lissie, Reynosa, and Upland Terrace Deposits of Coastal Plain of Texas between Brazos River and Rio Grande," *American Association of Petroleum Geologists Bulletin*, vol. 17, 1933, pp. 472-476.

¹⁰Price, W. A., loc. cit.

Formation of silica replacements.—Although our knowledge of the chemistry of silica and silicates is still somewhat limited, great advances have been made in recent years toward solving many of the perplexing problems presented by this class of minerals. Soil scientists have proved that there are two important agents which act most effectively to decompose silicates: (1) carbonic acid (H₂CO₄) and (2) the organic acids¹¹.

Carbonic acid results from the combination of CO₂ and H₂O; thus the opportunity for the formation of this acid is most favorable when there is a sufficient supply of CO₂ and H₂O. Such an optimum condition is to be found in areas covered by vegetation, for not only does the decay of the vegetation produce CO₂, but also small quantities of it are exhaled by the plant roots, and at night green portions of plants breathe out the gas.

Robinson¹² has demonstrated rather convincingly the effect of vegetation on the amount of CO_{\pm} in the soil air. He¹³ presents facts which indicate that: (1) soil air in vegetated areas, even in grassland regions, contains relatively large amounts of CO_{\pm} and (2) the quantity of organic accumulations in such areas, particularly in the grassy ones, is high.

The production of organic acids in a soil depends directly upon the amount of vegetational cover. It is apparent, then, that both carbonic acid and the organic acids occur in greatest abundance in regions covered with plant life. Since naturally vegetated localities (grasslands included) require relatively abundant precipitation (relative to that in arid and semi-arid regions), it is concluded that silicates will decompose most readily under relatively humid climatic conditions.

A. H. Church,¹⁴ in 1862, performed a rather unusual ex-

¹¹Clarke, F. W.: "The Data of Geochemistry," U.S.G.S. Bulletin 770, 1924, pp. 486-487.

Robinson, G. W.: "Soils Their Origin, Constitution, and Classification," Thomas Murby & Co., 1936, pp. 34, 41, 72-75. de Sigmund, A. J.: "The Principles of Soil Science," Thomas Murby & Co., 1935,

de Sigmund, A. J.: "The Principles of Soil Science," Thomas Murby & Co., 1935, pp. 13, 20.

¹²Robinson, G. W.: op cit., pp. 32-34.

¹³Robinson, G. W., *ibid.*, pp. 34, 41, 72-75.

periment relating to the replacement of CaCO₃ by silica. An aqueous solution of silica was allowed to filter slowly through a piece of modern coral. Eventually the silica almost completely supplanted the CaCO₃ of the coral mass.

In 1918 R. S. Dean¹⁵ also performed an interesting experiment pertaining to this same chemical phenomenon. Into a solution of silica which was saturated with CO₂ he introduced particles of CaCO₃ and CaCO₃-MgCO₃. Within an hour the silica was precipitated and the carbonates were However, when Dean tried the same experidissolved. ment with a silica solution devoid of CO₂, the silica did not precipitate until more than a year later. Dean explained the results obtained by advancing the following theory: The water solution containing the CO₂ formed carbonic acid, which upon coming in contact with the carbonate particles dissolved them. This reaction produced a bicarbonate solution whose cation $(Ca^{++} \text{ or } Mg^{++})$ caused the flocculation of the silica anion. The chemical equations for the reactions are:

- (1) $H_2O + CO_2 = H_2CO_3$
- (2) $H_2CO_3 + CaCO_3 = Ca(HCO_3)_3$
- (3) $Ca(HCO_3)_2 = CA_+ + 2HCO_3 CA_+ + 2HC$
- (4) Ca^{++} +silica anion=silica precipitate

Dean believes that some cherts may have been formed by such a process and suggests that Church's experiment might be explained on the basis of these chemical reactions. Barton¹⁶ also recognizes the possibility of calcareous fossils being replaced by silica in this way.

If it is assumed that the silicified fossils from the Finlay Mountains originated in the manner postulated by Dean, then certain questions regarding the silification process must be answered.

(1) What was the source of the silica? Since the rocks of the Finlay area consist almost entirely of limestones and shales, the obvious source of the silica is the

¹⁴Church, A. H.: (Title of paper not given), Journal of Chemical Society, vol. 15, p. 107. (Cited by F. W. Clarke, "The Data of Geochemistrv," U.S.G.S. Bulletin 770, 1924, p. 549.)

¹⁵Dean, R. S.: "The Formation of Missouri Cherts," American Journal of Science, vol. 195, 1918, pp. 411-415. ¹⁶Barton, D. C.: "Notes on the Mississipian Cherts of the St. Louis Area,"

Journal of Geology, vol. 26, 1918, p. 373.

silicates in the shales or in the insoluble residue of the limestones.

(2) Under what climatic conditions would silicates most readily decompose and go into solution? The importance of organic and carbonic acids in the decomposition of silicates has been discussed earlier in this paper. Since a relatively humid climate presents optimum conditions for the formation of these acids, such a climate would promote the decomposition and solution of silicates.

(3) What climate would be the most favorable for the replacement action as postulated by Dean? Again a relatively humid climate would prove the most favorable, for in such a climate the amount of CO_2 dissolved in the percolating ground waters would be at a maximum.

(4) Why, in general, are only the fossils replaced by silica and not the limestones also? The percolating ground waters which decomposed the silicates in the rocks of the Finlay area undoubtedly dissolved some of the limestone (CaCO₃) also. It would seem, therefore, that some silica should have been precipitated as the CaCO₃ dissolved. Perhaps the silicification of the fossils can be accounted for by the difference in the solubilities of CaCO₃, Ca(HCO₃)₂, and "silica precipitate."

(5) Why is the shell material silicified whereas much of the calcite in the shell voids remains unsilicified? The reason for this is not altogether clear. However, a difference in the solubilities of the calcareous shell material and the calcite in the voids may have caused the selective silicification.

Filling of shell chambers with calcium carbonate.—The time of formation of the $CaCO_{\pm}$ veinlets and that of silicification appear to be relatively recent. The dating of the period of filling of the shell chambers proves more difficult, however, for the chambers may have been filled at any time subsequent to the burial of the fossils. Therefore, the only definite statement that can be made regarding the age of this period is that it is older than the other two.

There is a possibility, though, that the shell chambers were filled recently. If this be the case, the calcite was deposited probably under arid climatic conditions, for it has been shown previously that such a climate promotes secondary CaCO₃ deposition.

Summary and Conclusion

Fusulinids embedded in the Permian limestone of the Finlay Mountains, Texas, exhibit one period of silicification and two periods of filling by CaCO₃. The chronological history of the fossils can be summarized as follows (Fig. 1):

(1) Burial of fossils in the Permian limestones.

(2) Period in which calcite filled the voids in the fusulinid shells. The only definite statement that can be made as to the age of this period is that it is the oldest of the three filling periods. If, however, the filling is of recent origin, then the process most likely operated under arid conditions.

(3) Period in which the fusulinid tests were wholly, or partially, silicified. Apparently the date of this period is recent. The replacement action is believed to have been accomplished by downward percolating ground waters under relatively humid conditions.

(4) Period in which fissures cutting across the silicified and unsilicified fossils were filled with $CaCO_3$ in the form of calcite and caliche. The formation of these veinlets is proceeding at present under the arid conditions existing in the Finlay area.

In the above sequence one, and possibly two, changes of climate are indicated for the Finlay area, the successive climates being arid, relatively humid, and arid. Interesting is the fact that Albritton and Bryan (personal communication) in working with soil profiles in the Davis Mountains, 250 miles southeast of the Finlay area, proposed a similar sequence of climatic changes for that region. It is possible that this similarity is merely coincidental; however, the close corroboration of the evidence from the fossils and from the soil profiles would seem to lend validity to the hypothesis postulated.

Fully recognizing the limitations accompanying this hypothesis, the writer wishes to suggest that periods of fossil filling and replacement may be indicative of past climates and climatic changes in an area.