STUDY OF LOCAL CONCRETIONS

by

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INTRODUCTION

A concretion (Twenhofel, 1926, Kindle, 1923) is an aggregate of inorganic matter in a nodular, discoidal, rhizoid, cylindrical, or other form within an enclosing rock. This, one of many definitions of concretions, is general enough to include nearly all things called concretions. It is too general to suit most authors. These aggregates of inorganic matter may include such substances as calcite, silica, iron oxides, siderite, pyrite, marcasite, gypsum, barite, aragonite, witherite, manganese oxide, calcium phosphate, fluorite, bauxite, and celestite. Concretions may be classified by method of growth, or by time of formation. Both of these classifications are objectionable. Concretions are usually restricted to sedimentary rocks.

There are a number of kinds of concretions in the vicinity of Manhattan. Simple clay concretions, segregations of calcium carbonate, are probably the most common. Translucent chalcedony nodules are often found on the hillsides. They are not agates for they have too coarse a texture. Geodes, hollow crystal lined nodules, are closely related to the chalcedony nodules. Concretionary masses of celestite, strontium sulphate, are fairly common in certain outcrops of the Elmdale Shale near Manhattan.

The iron sulphides, pyrite and marcasite, form small heavy concretions in the darker shales. Oxides of iron, usually limonite, form various rust-colored concretions. Flint or chert is common both in nodules and in beds several inches thick.

A number of types of concretions are not represented near Manhattan. Those fossil-containing concretions of coal beds are not present. Septaria, large vein-containing or divided concretions, also are not present. There are no local concretionary deposits of immediate economic value.

Because of their singular shapes, concretions probably have been noticed since the earliest human times. Early ideas concerning them are very much like the ideas suggested by uneducated people today. Absurd ideas are not limited to uneducated people, however. Commonly people will not accept the idea that concretions or beautifully shaped crystals can be of natural origin. Their conclusion is that the pieces were made by men and then lost. With a slight increase in knowledge, people begin to look for fossils. Concretions are soon found and identified as fossils of any object which they may slightly resemble. We have in our museum an object which was identified as a fossil of the large intestine of an elephant-like mammal. This valuable "fossil", probably of Cretaceous age, is a portion of a concretion containing radial crystals of calcium carbonate. We also hear of fossil toads, dogs, men, pumpkins, and walnuts.

REVIEW OF LITERATURE

General Literature

Reed (1931) states that a study of the history of geology shows that concretions have inherited the name formerly applied to all "shaped stones", and that the medieval explanation commonly given for such stones still colors most geological thinking about the origin of concretions. He further states that reputable geologists had begun to abandon the subject by the time they had tools with which to study it. He suggests that someone should do something now.

People have been working on the subject. A study of the literature shows that scientists have been checking their ideas with experiment for more than seventy-five years and they have accomplished much. This study also shows that many authors have written too much on incomplete or partial evidence. Some rather hasty statements have been made, and our modern literature contains its share. Reed's statements are essentially true, although it seems that some medieval thinking was very accurate.

Hayes (1857) reports some observations concerning the rapidity of growth of calcareous clay concretions. He found that concretions grew to the size of a garden bean during three weeks of wet spring weather. They grew in a rather permeable layer just below an abundance of calcium carbonate. He then discusses a law of restrained crystallization which accounts for the formation of nodules instead of crystals. The clay is considered responsible for the departure from the calcite crystal form. The clay was in the way.

Gratacap (1884) presents a good summary of earlier and contemporary thinking concerning concretions. Among the names which he has listed for them are clay dogs and clay stones. Because of great variety they are often considered mimics. "Concretionary action" has been held responsible for spherulites in lava, septaria in iron ores, flints in chalk, nodules in sandstone, "peastone" in limestones, hexagonal columns in basalts, the structure of granite boulders, segregations of iron pyrites, and clay concretions. An explanation of concretionary action is given:

> "Concretionary action has been assumed to indicate a cohesive and attractive property in matter when finely divided and when its particles possess some or considerable freedom of motion, whereby molecules of the same sort gather together in bunches or globes, sometimes coat over coat, the whole enlarging until the limit of cohesive action around that center has been reached, or the expanding circumference of one concretion meets and impinges

> upon its growing neighbors in a mass affected throughout by this toward-a-center movement."

A reveiw of literature is given.

Nichols (1897) states that clay stones are simply portions of the clay firmly cemented by crystals of segregated calcium carbonate. As a source for the lime which is segregated he lists: (1) Comminuted lime and calcite; (2) shells in situ; (3) comminuted land and water shells (glacial); and (4) mineral flour, especially lime feldspars. He states that the clays are not homogeneous for there are bedding partings, contraction joints, and tension planes which allow water circulations. Ground waters saturate the clays and carry the dissolved material. He says that, except for limonite, claystones are to be regarded as crystallizing aggregates whose growth has been modified by the large amount of foreign material (clay) present, and "the conditions of their formation are the same as those which would in more favorable positions lead to the formation of an aggregate of calcite crystals of the more usual form." Some rather good reasons for movement are given: the difference in solubility of calcite and aragonite, and the instability of humus acids. In the same solution aragonite could be dissolving and calcite could be precipitating.

Daly (1900) describes large, spherical, concentrically banded concretions of radiating calcite crystals. The concretions are one to three feet in diameter and are in a shale which contains enough organic matter to be inflammable. Numerous small pyrite crystals are also present. Daly endeavors to show that the large spheres developed after the shales were deposited, and he also selects a mechanism by which they could enlarge. The shale has two "extremely perfect" systems of joints at right angles, but they do not pass through the concretions. The strata arch over and under the concretions and "show clearly the effect of deformation along the radii of the equator." Slaty cleavage had developed in the shale tangentially to the concretions. The spheres are not perfect but are slightly flattened into spheroids. The author proceeds to disprove existing theories concerning the origin of these, and also presents one of his own. He shows that it is not a syngenetic concretion in shrinking strata. The idea of a preexisting cavity is considered invalid. That it is a pseudomorph after some other object does not allow enough volume change for the deformation of the shale, and the origin of the first concretion would still have to be explained.

The mechanism of enlargement which Daly presents is one which utilizes a volume change from the breakdown of a calcium bicarbonate solution. He does not allow the force of crystallization to do the work, for he says that it fails under laboratory tests. The total volume increase, liquid, gas, and solid, is what the author considers responsible for deforming the shale. Gas present causes increased capillary attraction which prevents the solutions from being driven out of the shale; otherwise the concretion would soon be isolated in impervious layers. It seems that the author allows crystallization of the calcite under pressure, although he does not admit force of crystallization. A certain amount of force would have to overcome the confining pressure.

Bell (1901) describes the large concretions of "Rock City" in Ottawa County, Kansas, as concretionary masses of crystalline limestone, mostly still in place. In the past these concretions have been considered to be glacial boulders, and one state geologist of Kansas described them as corals. These concretions, some of the largest in the world, (up to twenty-seven feet in diameter), are calcite and are cementing Dakota Sandstone. The Kansas Academy of Science is now working toward the establishment of a national monument in this area.

Cooke (1931) reports radial calcite concretions in the Marks Head Marl at Savannah, Georgia. Some of them are as much as two feet in diameter.

Mathias (1931) describes calcareous sandstone concretions in the Fox Hills Formation of Colorado. The concretions which he describes have Cretaceous plants (Halymenites major) for nuclei. Since the delicate stems of the plants are not crushed, it is suggested that the concretions formed very soon after burial of the plants, or partly before burial. Several methods of precipitation are suggested, including secretion of calcium carbonate by the plants during life, photosynthesis for a while after burial, and production of ammonium carbonate during decay. Precipitation during photosynthesis seems logical enough before burial, but the sand would have to be fairly transparent to allow much of it after burial.

Many other concretions containing fossils or just carbon are assumed to be due to some extent to the organisms. The commonest assumption and probably the correct one is that the formative reactions are due to the decomposition products from the organism. Thus black concretions containing silica and coarsely crystalline calcite are attributed to the fossilized sponges (Mathiasen and Schwartz, 1934).

Pyrite, as it occurs in sedimentary rocks, is often closely associated with organic matter and usually occurs in concretionary masses. It is found in dark shales and in coal beds quite abundantly. Schwartz (1927) tells of iron sulphide concretions from the Illinois coal fields. Some of these show well-preserved plant structures which may be examined in detail with the reflecting microscope.

Newhouse (1927) has studied iron sulphide and comes to the conclusion that the sulphide was a colloidal syngenetic deposit such as is forming in modern stagnant seas.

Feliciano (1924) describes coal-balls containing organic tissue. These concretions must have been formed in place, because projecting plant tissues are not broken. Sulphides of iron may have formed at the same time, or later, than the calcium carbonate. He discusses the methods by which ferric and ferrous sulphates may be reduced to ferrous sulphide.

Mathias (1928) discusses the evidence for the assumption that pyrite concretions are syngenetic.

Concretionary masses are reported in streams draining limestone regions (Stow, 1930, Roddy, 1915). Some authors object to calling these bodies concretions. Calcium carbonate is deposited upon any nucleus which may be present in these streams. In some cases the masses are considered to be formed by lime secreting algae, and in other cases the algae seem to be unnecessary. Algae are very likely to be present, however, because carbon dioxide is given off as the lime is deposited.

Reed (1926) reports aragonite in concretions from the Kettleman Hills in California. They have hollow cracked interiors lined with small platy crystals. He assumes that they have formed as a chemical precipitate when ammonium carbonate from organic decay reacts with calcium chloride and calcium sulphate solutions.

Binney (1923) reports cracked, hollow, calcareous concretions from Arkansas. They are called "oil cocoanuts" because of their size, their stems, and the fact that some contain as much as twenty c.c. of oil. The cracked interior is lined with calcite crystals. The oil is present simply because the concretions offered open collecting spaces.

Hamilton (1934) has used deformed calcareous concretions to estimate the changes during the metamorphism of a siltstone in South Dakota. Concretions which were once banded spheres of calcite are now ellipsoids of the size and shape of watermelons, oriented with the foliation of the rock. Some are seven times as long as their least thickness. They contain metamorphic minerals. Away from the zone of metamorphism the rocks grade into siltstone with spherical calcareous concretions.

Tucker (1922) reports large concretions, siliceous and calcareous, in the Knobstone Formation of Indiana. They are local and range in size up to a diameter of five feet.

Syngenetic Origin

Some of the earlier writers gave little consideration to the idea that many concretions may be syngenetic. Recently, however, a number of investigators have studied the evidence for syngenetic origin. There is some variation in definition of the term "syngenetic", however. It is sometimes hard to determine whether an author means an origin coinciding with the time of deposition of the sediments, or the formation of concretions during the lithification of the sediments. The first meaning would place a much narrower limit than would the second.

Tarr (1920, 1921) has offered as evidence of syngenetic origin the following situations: the composition when it is mainly clay and silica; the arching of beds over the concretions; the lack of stratification lines within the concretions; the lack of evidence of lateral crumpling of beds; slickensides, due to the consolidation of the beds around the concretions; large volume of the concretions; bands of concretions along bedding planes.

Physical Origin

Some writers have favored a mechanical origin for certain concretions. Gardner (1908) is one of the most widely known for this idea. In nearly every case this would mean contemporaneous or syngenetic origin. These "concretions" would be merely mud balls which have been deposited as a part of the sediment. They might form in rivers or in some near shore currents which disturb fine silts and clay. They would grow by accretion as they roll about, picking up pebbles and shells as they grew. In some sandstones the only portions which show fossils are argillaceous concretions. Where these fossils are in concentric bands it is probable that they were picked up by mud balls.

Haas (1927) has suggested that some mud concretions may have been formed by the rounding of blocks of clay in rapidly moving floods, and then the spheres were buried before they had disintegrated.

Kindle reports some large concretions in the Chemung of southern New York. They are large, ferruginous, blocky concretions weighing several tons. Along the bottom and curling up over the sides of these sandy concretions is a layer of fossils. The beds below and around these concretions are deformed. Kindle suggests that the formation of these concretions must have been at least partly physical, possibly due to gases escaping from the beds below. It seems, however, that overloading of sediments upon the band of fossils would have been sufficient. The fossil band would cup around the settling sediments, especially if the lower sediments were still soft and unconsolidated.

Cone-in-Cone

A curious feature usually found in calcite and often associated with concretions should be mentioned. This is a structure known as cone-in-cone, or tutenmergel. Tarr (1922) has given a very thorough review of the subject and has discussed possible origins and implications of the structure. It is probably worldwide in rocks dating from the Cambrian period to the present. It has been described as fossil wood and bone, and has caused much speculation.

As the name indicates, the structure consists of a series of parallel cones. Descriptions vary somewhat, depending upon the specimens examined. The bases of the cones may be in the same plane, or in successive planes. It is difficult to visualize from description, yet the phenomenon is easily recognized. Cone-in-cone occurs mainly as calcite on concretions, and also in beds. The calcite is fibrous, often horn-like in appearance. Clay impurities may be present between successive cones.

Much has been suggested concerning the origin of cone-in-cone during the last century. Tarr (1922) offers a list of references. Pressure is important in many of these theories. Crystallization is also an important part of some of the theories. Impurities have been considered the cause of imperfect crystallization (Keyes, 1896, Harnley, 1898). It has been considered to be related to stylolites. Pressure and solution working together may have caused the peculiar form. Recrystallization from aragonite to calcite has been held responsible.

Shaub (1937) observed conical sinks in recently deposited muds from which the water was draining. From this he has concluded that cups and cones could form during the escape of water from any highly saturated, porous, fine-grained sediment. He suggests that cone-in-cone associated with concretions is of syngenetic origin. Burt (1932), however, uses cone-in-cone and slickensides adjacent to the concretion to prove that external pressure caused cracking of the concretion.

White (1868) reports cone-in-cone in a radiating concretion with apices toward the center.

Tester (1926) reports the use of cone-in-cone in the correlation of Commanchean strata in Kansas.

Ferruginous Concretions

Iron oxide concretions are probably found in every country. They are abundant because iron is one of the common elements of the Earth's crust, and because the oxide is relatively insoluble. These concretions may be found where-ever the soil is red.

Wilcox (1906) reports iron concretions in the Redbank sands of Monmouth County, New Jersey. The concretions are most numerous in the upper part of the sand and may be isolated or grouped. The primary form is that of a long hollow cylinder. All cross-sections are circles or combinations of arcs of circles. Long axes of these cylinders are all parallel to the strike, but the dip of the rock is only slight. Fragile calcareous arborescent forms, "doubtless fossil stems of plants", ramify through concretions "in complete disregard of the interior partitions." He says that the concretions are clearly not crack fillings nor of stalactic origin, but are apparently formed in some way by diffusion. The sand is not so red near the concretions as it is elsewhere. At the outcrops the iron is often segregated into bands resembling bedding. The author suggests that the relationship to the strike is due to sorting of sediments near Cretaceous shores by waves. It would seem, however, that if it is the modern strike of the beds, there may be a relation between the concretions and the sub-surface water zones.

Cooke (1928) says that solutions tend to concentrate rather than to disseminate, in speaking of iron concretions and replacement.

Chert and Flint

Tarr (Twenhofel, 1926, p. 378-394, 509) has presented a thorough review of chert and flint. This concretionary type is of great importance and widespread occurrence. In this work the occurrences of chert and flint are given, with a review of the literature. Evidence of mode of origin are discussed in detail, and the need for more work is stressed. Masses of chert and flint are not necessarily concretionary, for where it is sufficiently abundant it occurs in beds.

Experimental evidence is cited to show that calcium carbonate in solution in the presence of carbon dioxide causes the rapid precipitation of colloidal silica, which would indicate that silica cannot be transported within limestones. Many investigators favor an epigenetic origin for chert and flint, which means that the nodules formed after the limestone was deposited. This question of movement of silica seems to hold the answer. In contrast to the evidence cited by Tarr, Lovering (1923) shows that silica is dissolved by calcium bicarbonate solutions.

Chert and flint are not the only silicious concretionary formations. Quartzites (Crosby, 1888) may be formed by the cementing of sandstones with silica. If this cementation is only local, concretions may be formed. They may be far from any igneous intrusion which could make them contact metamorphic deposits. Crosby (1888) describes quartzite lenses in fine Potsdam sandstone in the Black Hills of South Dakota. They are of vitreous texture, yet they are more like chert than contact quartzites. Organic silica is considered the source of silica. It is sufficient in these sandstones because they did not accumulate much more rapidly than a shale or a limestone. Ordinarily, sand grains are enlarged a little by reprecipitating silica. but there is not enough to form chert.

Brown (1929) reports centripetal concretions of silica, that is, concretions which appear to have diminished in size. He finds deposits or veins of silica along joints in limestone, and he finds small spherical concretions as evenly spaced as the centers of the joint blocks. He also finds intermediate siliceous concretions, and concludes that the silica deposited along the joints migrates inward as a shrinking concretion.

Silica, in its characteristics and relationships, presents an interesting problem. Rogers (1928) summarizes the characteristics and relationships of the various forms of silica. He discusses the naturally occurring forms of silica, their temperature relationships, and the possibilities of one form altering to another. Hayes (1897) reports cases where quartz pebbles in exposed conglomerate are very deeply etched by solution. As the occurrences are too widespread to be due to thermal or alkaline waters, Hayes suggests that a buried and constantly moist pebble could be dissolved much more rapidly.

Lovering (1923) gives the results of experiments concerning the solubility of various sources of silica in solvents. He has done this work because of apparent inconsistencies in the literature. Ideas differ about the solubility of silica. He shows analyses of natural waters which are known to contain silica, and then makes up solvents suggested by these solutions. He then shows their solvent action on powdered minerals. He powdered quartz, jasper, taconite, greenalite, opal, actinolite, chalcedony and glauconite. All were attacked by sodium hydroxide, as were the pyrex containers.

A mixture of sulphuric acid and sodium chloride attacked silicates, but not silica; magnesium bicarbonate attacked everything strongly, while calcium bicarbonate attacked everything, but not so strongly. Sodium carbonate was a fairly effective solvent. Magnesium sulphate reached equilibrium quickly, and mixtures with magnesium sulphate reacted in much the same manner. Sodium chloride had some action on silicates but probably no more than pure water. Humic acids, from peat, caused the appearance of silica in the blank as well as over the powdered minerals, but it appeared more slowly in the blanks.

Lovering's conclusion is that silicates are attacked by acid solutions, and opal and chalcedony are attacked by alkali; quartz, jasper, and taconite are attacked best by bicarbonates. In his attempts to precipitate silica, he was unable to duplicate Tarr's precipitation of silica from artificial river water by artificial sea water; however, he used natural sea water instead of artificial sea water. He was able to precipitate silica from concentrated solutions with a small amount of sea water, but he found that greater quantities of sea water only made the solution more dilute, with less precipitation resulting.

Hubbard (1922) discusses the importance of the study of colloids to geology. He gives considerable attention to colloidal silica. He outlines the earlier literature of silica experiments: crystalline quartz has been formed from silica solutions. He discusses diffusion and reactions of impurities in silica gels, and Liesegang rings. He discusses the flocculation of sediments with electrolytes, comparing NaCl with $AlCl_3$ and $Al_2(SO_4)_3$. He also discusses the colloidal formation of iron ores and bauxite.

Geodes

Geodes are very closely related to concretions. Some authors make no effort to separate geodes from concretions, yet other insist that there is a significant difference.

In America the best known and the most typical geodes are those of the Keokuk beds. These geodes have long been known, and many efforts have been made to explain them, In 1871 Perkins gave a very detailed description of these geodes. He mentioned an aluminous layer on the exterior and free quartz crystals on the interior. As an origin he suggests that the beds were once a plastic mass of clay in which bubbles of gas accumulated. These bubbles were soon filled by solutions of silica which crystallized before the solidification of the mass.

In 1878, Wallace presented an idea based on a fossil origin of geodes. Wallace, noting the peculiar shapes of the various geodes, decided that what they most resembled was a sponge. He observed the way the geodes were scattered through the rock. Since he found no points of attachment, he decided that they were drifting sponges. He named the genus "Biopalla." He then named eight species, for all the geodes did not look the same. His sponges drifted about on the sea floor until a group of them were overwhelmed and buried in mud. They were then fossilized. When the surrounding rocks were hardened, solution removed the sponge, leaving only the cavity where it had been. The cavities were then lined with chalcedony, quartz, and calcite. After the first formation of the geodes, the shales were greatly reduced in thickness, possible by weathering. "The shale seems to be but the remains of original deposits several times thicker." During this reduction and compaction of the shale some of the geodes were crushed, but were later relined with unbroken layers of crystals. Many of the geodes are so close together as to be angular in shape.

Van Tuyl (1912, 1916) has given what is probably the most complete study of these geodes in recent years. He describes them and reviews previous ideas concerning their formation. In diameter they range from 1/16 inch to thirty inches. They are siliceous and calcareous, with pyrite, sphalerite, aragonite, gypsum, limonite, malachite, smithsonite, kaolin, dolomite, and magnetite. In some specimens there are two distinct generations of mineralization. He reviews a number of interesting ideas. The geode cavities have been thought to be due to gas bubbles in once-molten rock. The geodes have been called meteorites. The sponge fossils are mentioned. According to Van Tuyl, bubbles of carbon dioxide in marl, while Mooers suggests the oxidation of organic matter to leave a cavity. He also mentions Shaler and the fossils in the Knobstone of Kentucky. Those fossils have been shown to develop into geodes by vein enlargement.

Van Tuyl says that the geodes show no relationship to the weathered outcrop or to accessibility of water, and that there is no evidence of increase of size. His geologic column, however, shows four disconformities in the Mississippian beds imediately above the geodes. This, together with Wallace's opinion that the beds are residual from much thicker beds, would indicate that the entire beds have been closely related to a weathered outcrop and to accessibility of water.

Van Tuyl suggests that the geodes have formed around syngenetic calcareous concretions which have later been dissolved away. The sequence of events which he gives is as follows: the calcareous nodules grew and were buried; a siliceous shell was deposited; then the calcite began to dissolve away; minerals were then deposited within the siliceous shell. Van Tuyl says that the geodes undoubtedly grew below groundwater level, while solution of nodules was above groundwater level. Bitumen, present in some, must have been added later, for it has not interfered with geode growth. The mineralogical character is quite variable, especially in different localities.

Quite in contrast with Van Tuyl's idea of the relation of the geodes to the groundwater level is an observation by Hunt (1880) thirty years earlier. He shows silicification of logs above the drainage level in fairly recent sediments, while the logs below the drainage level consist of lignite. The silicification in the weathered zone above drainage level could have changed, but it is difficult to say that the quartz "undoubtedly" grew below groundwater level.

The reports of earlier observers would also indicate evidence of possible enlargement of the geodes, while Van Tuyl says there is none. The aluminous layer (Perkins, 1871) on the outside could be residual clay left from dissolved matter, or else clay compacted by a growing geode. The billowy form which has been so carefully described (Wallace, 1878) would hardly have been present on the original calcareous nodules; it would suggest expansion. The geodes are also reported to be closely packed together in beds (Wallace 1878), so much so that a hexagonal form has been assumed. If the original calcareous concretions were so closely packed, the entire mass would have probably become one large geode. Recently a similar but more extreme packing of geodes has been reported (Osinski, 1934) just below the middle of the Harrodsburg Limestone in Indiana. Some geodes in this bed are not crowded and are nearly spherical; however, there is a lens of faceted sliver-like wedges, each a complete geode. The mass of geodes has a striking resemblance to cone-in-cone structure. The large ends of these cones or wedges are portions of spheres.

LOCAL CONCRETIONS

Calcareous Concretions

In the mantle rock and unconsolidated sediments of any region which is not deficient in calcium carbonate there may be typical clay concretions. Included among these are loess concretions. These are peculiarly shaped nodules containing clay, silt, and sand cemented with calcium carbonate. The percentage of calcium carbonate is variable, depending upon initial pore space and other factors. The color may be a lighter shade of the color of the surrounding material. Near Manhattan are yellowish, brown, and white concretions of this type. They are usually spheres or aggregations of spheres with diameters varying from one-fourth inch to three inches. Nearly all of these concretions show a combination of fractures on the inside. These inner surfaces may be lined with small, clear calcite crystals.

Most observers agree that the interior cracks indicate shrinkage of the interior after hardening of the outer wall of the concretion. Loss of water is the explanation offered. Some observers have considered the cracking of similar concretions to be due to growth and enlargement of the outer shell.

The indication of shrinkage suggests that the calcite was originally deposited as a mass of fine colloidal or nearly colloidal particles. The translucent appearance of some of the most recently formed concretions also suggests colloidal nature. Colloidal particles absorb large quantities of water with dissolved material. A colloidal aggregate that is very fluffy at first will in time give up water and become more compact. Adsorbed calcium bicarbonate might aid in forming a calcium carbonate cement. Microscopic examination shows that these concretions are not composed of colloidal calcite now, but of fairly large crystals with inclusions of sand and clay. Rapid deposition may result in crystals of very small size, and more time would allow alignment and recrystallization. Possibly a few weeks of wet weather would be sufficient for the deposition of a mass of fine calcite. Subsequent years would allow recrystallization.

Such concretions should be formed wherever groundwater can bring dissolved calcium salts into a zone where they can be rapidly precipitated. Precipitation may be near the surface by evaporation. Warm layers near the surface may make calcium bicarbonate unstable. Soluble calcium salts may be precipitated by a carbonate ion. Loess concretions near Manhattan are in zones which could afford rapid precipitation and sources for calcium are readily found. The loess is very permeable and allows ready circulation of water. Similar concretions are found in the soils near or on limestones. Many of these concretions may be redissolved each year and new ones may be deposited; thus, such a concretion might be a year old, or thousands of years old.

Ferruginous Concretions

In the lower Elmdale Shale and in the Admire Shale east of Manhattan there are deposits of iron sulphides. They are nodular masses of pyrite and marcasite crystals. Both of these minerals have the formula FeS_2, but the crystalline structure of pyrite is isometric and its color is a brassy yellow. Marcasite is orthorhombic and of a greenish yellow color. Pyrite is heavier than marcasite. Determination of crystal structure by X-ray is the most certain means of identification, but these concretions have not been so examined. These concretions are not much more than an inch in diameter. They are flattened spheres with impure shaly equatorial or bedding plane extensions. The concretions have a specific gravity of about 4.8, slightly less than the specific gravity of pure pyrite. In a damp atmosphere the minerals oxidize rapidly, and the odor of sulphor dioxide is usually present. Sulphates form and hydrous iron oxide is left in the concretion.

These concretions of iron sulphide are found in sandstones and limestones, but they occur most frequently in shales containing an abundance of organic matter. They are protected from oxidation in the impervious shales, but in some limestones and in most sandstones they are rapidly oxidized. Black organic matter is an indication of little oxidation. Probably sulphides develop best in sediments containing an abundance of organic matter (Mathias, 1928). Decomposing organic matter gives off reducing gases, hydrogen, methane, and hydrogen sulphide. Hydrogen sulphide will precipitate ferrous sulphide from solutions of iron salts.

The colloidal precipitates which are found on parts of the sea floor today may compact and recrystallize as pyrite or marcasite. Reducing gases and reducing bacteria would tend to change ferrous sulphate to ferrous sulphide. Iron oxides and sulphate minerals may be evidence of former iron sulphides.

Limonite, a hydrous ferric oxide, is common in weathered rocks of Kansas. Limonite, like silica, is soluble only under certain conditions, and much of the time is fairly insoluble. Iron solutions from the decomposition of pyrite may move for some distance and be precipitated when they are neutralized by calcium carbonate. Iron becomes concentrated in residual sediments because it is rendered temporily less soluble than surrounding material. Thus the outcrop of Dakota Sandstone in Kansas may be very ferruginous, but the same beds are much lighter in color away from the outcrop. Concretions in this sandstone attain very fantastic shapes. They combine hollow spheres, cylinders, and boxes to make strange shapes. Within the hollow center is loose sand which the microscope shows to be of the same nature as that in the walls of the concretions. This sand is relatively free from the colored iron oxides. The walls are made up of one or more firmly cemented bands of sandstone. These cemented bands are concentric and resemble the phenomenon which has been termed rhythmic precipitation, or rhythmic banding. It may well be a case of rhythmic precipitation, but the problem is the source of the iron. If the present concretion was once a mass of rather calcareous sandstone, then the water carried by this sandstone would deposit its burden of iron and carry away a more soluble salt of calcium. It can be easily demonstrated that calcite will precipitate iron compounds from acid solutions of iron, and the precipitate will form immediately around the calcite.

Ferruginous sandstone concretions may form in other ways. Some rather impermeable specimens of sandstone have been known to contain pyrite which could readily alter to limonite. The Dakota sandstone is an aquifer; that is, it transports rainwater underground. Rainwaters contain a considerable amount of free oxygen in solution. This oxygen is removed by any mineral or organic substance which will oxidize under ordinary conditions. Pyrite is a mineral which will oxidize readily, especially if it occurs in rather impure concretions. The first products of oxidation, iron sulphates, are soluble and can diffuse outward, or they may be carried along by circulating solutions. Indeed, the solutions may be capable of dissolving already precipitated iron and carrying it farther. Eventually, however, the sulphates will be precipitated by reaction with some other compound, probably calcium carbonate. Each additional supply of freshly oxidized material may push the wall of precipitate farther. Diffusion acting alone for transportation would tend to produce cylinders. Diffusion along joint cracks would cause the formation of angular boxes. Concentric layers could be due to the diffusion of one of the reacting solutions through previously formed walls of precipitate. This could mean that carbonate solutions are closing in on the source of the sulphates, or it could mean that each new advance of the sulphates was able to go a little farther before precipitation.

Limonite has been collected from a number of residual, colluvial, and alluvial deposits near Manhattan. These types of deposits are all closely related, and are also related to the deposits of glacial material. Similar small limonite concretions are found in all of these types of deposits, and may all be of similar origin. Residual materials upon the hills near Manhattan may have supplied much of the local stream and glacial deposits. All are characterized by gravel, consisting of chert, limonite, and clay. Residual soils are concentrations of the least soluble materials of the former bedrock. Thus, limonite is found mixed with siliceous material and clay.

Most of the limonite pieces are small, flat, and highly polished. When broken, they appear to be uniform in composition. Some of them are hollow. They may have one or more sets of walls. Most of them are angular in shape, suggesting broken fragments of a larger object. They may contain sand, clay, or both sand and clay.

Among the limonite concretions are a few which deserve especial mention. They may indicate the origin of the residual limonite. Some of the complete concretions resemble well-known Permian fossils, but the lines are bulging and exaggerated. Closer examination reveals that these concretions are masses of limonite with a fossil for a nucleus. The most easily recognizable of these are brachiopods, although the species may be doubtful. Three out of less than one hundred specimens show approximately the same origin, while the rest indicate very little. Some of the others are just fragments. The unbroken concretions from temporary stream sediments show little evidence of having moved very far since their formation. They seem to have been but recently removed from the creeping mantle. The fresh, unbroken appearance of the concretions seems to indicate also that they but recently attained their shapes.

The fossils within these concretions appear to be hollow with a thin siliceous shell. Whether the original fossil was calcareous, siliceous, or pyritized cannot be well determined. If it was calcareous, then the iron solutions from the surrounding soil would have tended to deposit upon it because of the greater alkalinity. The only reasons for deposition of limonite upon a siliceous fossil would be the action of colloidal silica as a catalyst or as an adsorption surface. If the fossil was pyritized as fossils sometimes are, then the problem is simply one of oxidation, followed by precipitation upon contact with the outer solutions.

Siliceous Concretions

Flint and chert are abundant in the hills of this section of Kansas. The Flint Hills south of Manhattan are covered with broken fragments of this sedimentary rock. The flint does not comprise a very large proportion of the total sediments, but it is resistant enough to weathering that it is prominent at the surface. The surface of a nodule two inches across is usually white or gray and is rather porous. Colors are usually concentric, and just inside the surface band there may be one or more zones of darker color, either black or brown. The center portion is uniformly brown, gray, or nearly black. The fracture is conchoidal, and the broken edges are very sharp. Fossils are common in the flint. Many of the siliceous fossils are forms which, during life, had shells of calcium carbonate. They were silicified after death, possibly only a short time after death. They are very well preserved.

Nodules and fragments which have been exposed longest to weathering show the greatest development of the white porous surface. It is probably that in these cases the porosity is due to weathering, especially by solution. It has been suggested, however, that this banding may be due to recent growth of the concretions. Chert nodules in outcrops of the Cottonwood Limestone north of Manhattan have been weathered so extensively that the porous material now extends to the center. They are very light in weight when dry. The positions of the nodules and the fossils in them indicate that the chert was deposited at nearly the same time as the limestone. The chert nodules occur in beds within the limestone. Recent deposits of chalcedony do not follow the bedding planes. The flint or chert, as it weathers, liberates large amounts of silica. We should expect to find siliceous deposits below any weathered bed of flint, because the dissolved silica probably is precipitated after being carried a short distance.

In solution channels in the Cottonwood Limestone long tubular "pipes" of chalcedony and quartz are deposited. It is likely that the dissolving chert supplied the silica for these deposits. Siliceous groundwater solutions probably do not penetrate far into the limestone before the concentration of dissolved salts exceeds the precipitation point for most of the silica.

Chalcedony nodules, many of them geodes, are very common in the mantle rock for at least two hundred feet above the Cottonwood Limestone. Flint or chert is even more abundant. This chalcedony is rather coarse and may be bluish gray, white, or red. Quartz or calcite may be present.

Well developed geodes are found just above the most resistant beds of rock. They may be easily found by examining a road cut above such a rock as the Cottonwood Limestone and only a few inches below the topsoil, large geodes of chalcedony lined with calcite are common (Fig. 1). Several factors might cause this concentration of geodes in such local areas. Some authors argue that weathering has little to do with the distribution of the geodes, that the geodes or the cavities containing them were parts of the original characters of the rock. They further argue that geodes must of necessity be formed below the water table, and that the hollow part must be filled with groundwater (Van Tuyl, 1916). Near Manhattan the geodes are above the water table or very near the top of it. Of course the water table may not be near its past locations now. Groundwater is forced much nearer the surface at the Cottonwood Limestone outcrop than it is immediately above. An increased amount of vegetation gives evidence of this. The outcrop of Cottonwood Limestone may be traced for miles in the hills by the dark line of vegetation which it shelters and supports. It may be largely a factor of time which allows the growth of geodes. A table of nearly level rock, being a natural erosion control, might allow greater weathering and a longer time for deposition than would a sloping hillside. Thus geodes would have a longer time of formation than elsewhere, and so would a supporting soil for plants.

Within the Elmdale Shale is a calcareous portion about twenty feet thick. Prominent in fresh cuts through the shale at this level are nodules containing coarsely crystalline celestite. These nodules range in size up to a diameter of four inches. The crystals may have well developed faces, or they may be closely crowded together. The color of the mineral is a pale blue-gray, except where there is iron-staining. Chalcedony, easily determined by its hardness, is usually present where a red color is noted. Sometimes red celestite is observed, however, Calcite may be interspersed with the celestite crystals, making the mass solid.

Where this portion of shale is moderately weathered and has become part of the subsoil (Fig. 2), we find peculiar calcite geodes instead of the celestite nodules. The calcite is present as small, clear, well developed crystals, or as radiating aggregates of white fibers. Chalcedony is present in these geodes, either white or red, but celestite is rare or absent.

In certain places outcrops of this calcareous portion of shale may be found buried beneath a few feet of material which was deposited during, or perhaps later than, the age of Kansas Glaciation. Under these relatively ancient sediments an old weathered soil may have been buried. The age of the buried soil is dated (Fig. 3). In parts of these old buried soils which are residual upon the calcareous zone of Elmdale Shale, the celestite is absent, and the calcite geodes are no longer noticeable. Instead of these tiny geodes of chalcedony and quartz may be crowded together in bedding planes. Nearly two hundred of these were obtained from a limited zone two inches thick and eight inches square. In the few places where these geodes have been found, they are seldom more than one-half inch in diameter. Some of the smallest, no larger than match heads, are nearly all chalcedony and are not hollow. Quartz may be present as small clear patches in these tiniest geodes, while in the larger half-inch geodes the entire lining of the cavity may be of clear, sparkling quartz crystals. Smaller geodes than these may have escaped detection.

Calcite is present in these geodes. In some cases it occurs as tiny pseudo-cubical crystals upon the surface of the clear quartz crystals. In more rare cases calcite composes part of the geode wall, as one or two yellowish crystals, greatly etched. In some of the smaller nodules, chalcedony nearly surrounds one large crystal of calcite. Sometimes calcite occurs as a single large crystal in a cavity just large enough to contain it, and no chalcedony is present.

The fact that these quartz geodes have been found only in limited areas does not mean that they do not occur elsewhere, but it may indicate that the conditions for their formation are rather limited. The soil in which they were found was apparently weathered before glacial times, and solutions near the surface have been active in it since that time. Other soils probably do not last so long, especially on these hillsides. Slow but constant erosion and soil creep does not allow prolonged weathering on a sloping surface. Road cuts and steep cliffs cut by meandering streams offer the best chances for fresh exposures of relatively unweathered shale; thus, the east side of Bluemont Hill (NE$\frac{1}{4}$ Sec. 7, T. 10 S., R. 8 E.), the north end of Mount Prospect (Sec. 20, T. 10 S., R. 8 E.), and Cedar Bend (NW$\frac{1}{4}$ Sec. 13, T. 10 S., R. 8 E.) show the freshest Elmdale Shale. There are rock exposures which show three distinct ages of weathering. One type has been weathered only a few years, another has been weathered thousands of years, and the other hundreds of thousands of years. It is not so strange that in these three types of exposures of the same shale we find three different groups of concretionary bodies. A time relationship may exist between the different groups of minerals.

Celestite seems to disappear first from the rock. Although it is so concentrated as to make up concretions in local beds of shale, the total amount of celestite is a very small proportion of the total rock. While celestite is not very soluble, calcite is much more abundant. Rainwater may be quickly saturated with calcium carbonate long before it reaches the celestite containing beds, but it does not have to remove very much celestite after each rain to remove the entire quantity in a few years.

Thin sections have been made from the nodules of the Elmdale Shale, especially the small quartz geodes and related nodules. These sections have been studied with the aid of a petrographic microscope. These small geodes are of interest because an entire section can be placed on one microscopic slide, and the mineral relationships are quite evident.

Chalcedony is present in every specimen. The chalcedony is composed of microcrystalline silica with radiating clusters of thread-like crystals. In the larger geodes chalcedony is present only in the outer crust, but in the smaller nodules it may extend to the center. The chalcedony is white by reflected light, showing some red spots. By transmitted light it is brown, with bands of darker color. The bands are concentric, but not necessarily concentric around a central cavity. Usually the bands are normal to the fibrous crystals. Quite frequently the bands of chalcedony are concentric around clear quartz crystals which are scattered through the mass. In such cases the bands nearest the crystal will follow the angular outline very sharply. The bands are incomplete at the inner side of the chalcedony wall, trailing off into clear quartz. In some specimens the bands are also incomplete at the outer surface, but this may be due to weathering. This close relationship between the crystals and the bands suggests that the chalcedony is recrystallizing as quartz, or is being replaced by quartz. The alignment of the chalcedony bands with the quartz crystals could be the result of deposition of chalcedony upon quartz, except for the incomplete bands. The incomplete bands of chalcedony show that quartz may start to develop in the chalcedony, forcing impurities out into dark bands just beyond the forming crystals. As long as the forming crystals are completely surrounded by chalcedony they are completely surrounded by the darker bands. The chalcedony is limited, however, and eventually a growing cluster of quartz crystals may extend beyond the original chalcedony. When this happens, the bands of impurities will be broken and incomplete, but will continue to be pushed outward through the remaining chalcedony (Fig. 14-17). By this theory smaller crystals should be surrounded by more and heavier bands. This situation is demonstrated by microscopic study (Fig. 10). If the chalcedony had been deposited upon the crystals of quartz, the bands should have been continuous, and of equal size over large and small groups.

As has been suggested, quartz in these nodules occurs in two distinct ways. Clear quartz lines the interior cavity and scattered crystals and aggregates occur throughout the chalcedony. Crystal faces are easily recognized as prisms and pyramids, although the crystals are of very small size. Single small crystals no longer than one-half millimeter may lie loose within the interior cavity. The quartz in some of the geodes is white and clouded with tiny inclusions or with tiny angular cavities. An outer layer of the crystals, however, is clear. Growth lines are common.

Occasionally a small chalcedony nodule will be a shell, the inside of which is entirely filled with a crystal of calcite; or, more likely, it is a crystal of calcite coated with chalcedony. Sometimes hollow chalcedony nodules show an angular cavity such as would have resulted from the solution of a calcite crystal. It is easy to see that some geodes could be formed by the relining of such a cavity (Van Tuyl, 1916). Where there is no calcite or other easily soluble mineral, however, such a mode of origin is less likely.

Description of Slides

Fifty-three thin sections of the small quartz geodes were studied carefully. Every one of them showed chalcedony at least in the outer wall. Nearly all specimens showed fairly good crystals of clear quartz. A few showed calcite, but calcite was lost from some specimens during the process of slide-grinding. The sections vary somewhat in thickness. Each section, of course, represents only one of many possible sections of one geode. The sections are numbered consecutively G1 to G53.

Slide G1 is typical; it shows chalcedony and quartz. The chalcedony is banded, the bands running around good sections of quartz crystals. With crossed nicols the banding is obscure, lost in radiating needle-like microcrystalline quartz. These radiating fibers are generally normal to the banding. The bands follow closely the angular crystal outlines, the bands nearest the crystal being angular (Fig. 4). The inside of the geode is composed of quartz, the crystal faces well formed. There are many inclusions of small quartz crystals within the larger quartz crystals. Good optic axis interference figures were observed in the quartz of this geode. The clear quartz of the crystal faces is a thin layer over the inclusion-clouded quartz.

Slide G6 shows most of the characteristics of slide G1, except that the quartz shows tiny cavities instead of inclusions. The cavities give a weathered appearance to the quartz. There is no definite contact between the chalcedony of the outside and the quartz of the inner layer. Quartz crystals may be hald in the chalcedony as if they were rooted in it. One such crystal (Fig. 5) has one of its pyramids surrounded by chalcedony; the other end is surrounded by clear quartz. The end which is buried in chalcedony is surrounded by bands parallel to the crystal surfaces. Similar bands are inside the crystal. The bands, instead of running all around the quartz crystal, stop approximately at the boundary between the chalcedony and the quartz. This termination of chalcedony bands in quartz seems to show that the quartz is growing in the chalcedony.

Slide G11 shows chalcedony banded around centers, usually quartz crystals. Along the margin between the clear quartz and the brown chalcedony is a hexagonal section of quartz, half in quartz and half in chalcedony (Fig. 6). The brown of the chalcedony, however, has been concentrated in narrow, dark bands between clear bands of quartz. The hexagonal outline is continuous.

Slide G16 shows banded chalcedony and clear quartz. Some of the bands are incomplete, ending in quartz. The quartz is especially interesting in this slide because there is a definite change from the older white or etched quartz, and the most recent, or clear quartz (Fig. 7). Crystal faces show distinctly, and the quartz is free from cavities and inclusions to a depth of 1/64 inch. Below that depth all the quartz is rough and etched.

Slide G17 shows a number of quartz crystals which have started to develop on the inner edge of the chalcedony and have continued to grow into the chalcedony as well as out from it (Fig. 8, 9).

Slide G21 shows very well the relation between the radial clusters of quartz and the chalcedony. In one area (Fig. 10) there are two radial clusters not far apart; one of them is 1/32 inch in diameter, and the other is about 1/80 inch in diameter. The larger cluster is surrounded by four distinct bands of chalcedony, which increase the diameter of the group to 1/16 inch. The smaller group is encircled by but one band, which follows the outline closely. Apparently the larger cluster has been able to force more of the impurities out into bands because it occupies a much greater volume of the chalcedony. The smaller cluster has not reached that stage of growth. The chalcedony not affected by quartz crystals is not banded and shows no evidence of disturbance.

Sections which show chalcedony banded around quartz crystals are G1, G2, G6, G7, G9, G13, G14, G16, G18, G4, G21, G22, G24, G25, G28, G29, G30, G32, G43, G45, G46, and G47 (Fig. 4, 10, 11, 12, 13, 18, 19, 20, 21).

Chalcedony with bands incomplete is well shown in slides G6, G7, G11, G15, G16, G18, G23, G24 (Fig. 5, 6, 13).

Quartz with inclusions or rough etched appearance is shown in slides G1, G6, G11, G16, G17, G35, G44, G45, and G46 (Fig. 7, 8). Quartz which shows growth lines, including chalcedony bands, is seen in G4, G11, G17, G28, G29, and G31 (Fig. 5, 6, 8, 9). The geode section G8 shows no clear quartz, but is all chalcedony.

The microscope has shown that quartz crystals are growing in the solid chalcedony. Whatever the method of growth may be, it seems that eventually a number of radial aggregates will be touching. If there is growth pressure in crystals, it seems that the aggregates will be forced apart, leaving a cavity in the center.

Solubility Experiment

The effects of various solutions upon geode fragments have been studied in a solubility experiment. The solutions were allowed to react for two months, and the results are based upon changes of weight of the geode fragments as well as tests for calcium and silica in solution.

All of the geode fragments were taken from one large geode and each fragment contained both chalcedony and calcite. Each of the fragments weighed nearly twenty-five grams and the surface areas were roughly equal. The fragments had reached a uniform weight after being dried for a total of thirty-six hours. All had previously undergone the same conditions of weathering and it is assumed that they would have reacted similarly in the same solutions. Glass bottles from the same lot were used as containers. The fragments were immersed in the various solutions for two months, and at the end of that time the tests were made.

The experiments were designed primarily to show the relationships existing between silicic acid (Baker's lot 61437) and the minerals of the geode fragments. About five grams of dry silicic acid was added to 400 c.c. of water in each container, and other reagents were added in some of the experiments. A system of blanks was arranged to aid in the interpretation of the results. Four containers were used for each reagent. For example, one bottle contained water, sodium hydroxide, silicic acid, and a geode fragment. The next bottle was a duplicate except that it did not contain a geode fragment. The third bottle contained sodium hydroxide, water, and a geode fragment, and the fourth bottle contained only sodium hydroxide in water. Other sets of four experiments used as reagents sodium bicarbonate, magnesium oxide, and a mixture of magnesium oxide with sodium bicarbonate. One set of four containers used only water and silicic acid with the geode fragments (Nos. 29-32, Table I). Containers number thirty-three to thirty-six have used only sodium silicate (Coleman and Bell Co.) in water, except that numbers thirty-five and thirty-six were neutralized with hydrochloric acid.

It was necessary to use care in handling the geode fragments, for small pieces might have broken loose. All such pieces were saved when it was possible.

A loss of weight may have meant breakage, but such loss was guarded against. A loss of weight probably indicates solution of one of the minerals; thus, in number twenty-nine, there is recorded a loss of 0.0606 grams, the only major loss in weight. Since silicic acid was the only reagent, the suggestion of solution is strengthened by the appearance of calcium in the solution, as shown by the oxalate test. A smaller loss was recorded in number thirty-one, where only distilled water was present as a solvent. In this case both calcium and silica were recorded as faint traces in solution.

Simplified chemical tests were possible in these experiments; conditions were known and interference was minimized. As a test for calcium, one-half c.c. of ammonium oxalate solution (4%) was added to one c.c. of the solution to be tested. Nearly all the solutions were basic, so precipitation was immediate. To test for silica, a modification of the molybdate test of Engelder's Semi-Micro Qualitative Analysis was used. To one-half c.c. of sample acidified with HCl a drop of ammonium molybdate solution was added. If silica was present in appreciable quantities a yellow color developed. A drop of benzidine hycrochloride solution was then added, and a white precipitate formed. Upon the addition of ammonium hydroxide a blue precipitate formed. The intensity of this blue was used to estimate the amount of silica in solution. An intense blue indicated between two percent and 0.02 percent silica. This has been called a "strong" test. A "moderate" blue indicates somewhat less silica, and a trace of blue means really a trace of silica. The test for calcium was not so delicate as was the test for silica. Care must be used in this test for silica, since other substances interfere greatly. In testing unknowns, interfering substances must be removed without removing the silica.

In case of replacement of calcite by silica the difference in weight would be very little. Calcite is very slightly heavier than silica; therefore, complete replacement of calcite by silica would cause only a minor decrease in weight.

Increase in the weight of some of the geode fragments (Nos. 1, 15, 25, 27, 33) does not mean molecular replacement. It could mean crystal growth, or simply adsorption, or both. Geodes in numbers one and three showed an efflorescence when they were dried, but only one showed in increase in weight. The silicic acid seems to have made the difference. In number one the solution was saturated with silica, apparently.

Some of the silica may have been added to the fragment. Silica may have been removed from the fragment in number three. The chemical test has shown that considerable silica was dissolved, but from the bottle as well as from the geode.

Containers twenty-nine to thirty-two showed silica in solution whether silicic acid had been added or not, but number twenty-nine, with both silicic acid and a piece of geode, showed the greatest quantity of silica. Apparently the calcite present increased the solubility of the silicic acid. Calcite was dissolved from the geode both in the presence of silicic acid and without it, however.

The weight increase in number fifteen is most easily accounted for by adsorption with some possibility of precipitation and replacement.

Since numbers twenty-five and twenty-seven gained weight regardless of the silica, it seems likely that the gain was due to some precipitation from the mixture of sodium bicarbonate and magnesium hydroxide. The sediment in the bottom of the container was very stiff, apparently cemented.

Other changes in weight are not very great, although they may be significant. The changes may be seen in Table I, but it is suggested that more work should be done with these solvents before definite conclusions are drawn.

The appearance of traces of silica in numbers twenty-two and twenty-four, but not in twenty-one and twenty-three is rather interesting. Apparently the presence of the geode suppressed the silica in solution; it may be, however, that some impurity supplied by the geode interfered with the chemical test.

All the geode fragments were examined carefully to determine any evident changes. The fragments from containers five, fifteen, twenty-five, twenty-seven, and twenty-nine had held slight coats of powder. The fragments from containers one and three effloresced with a white powder as has been mentioned. It will be noticed that some of the fragments which gained weight are those with the adhering powder. But two of those with powder actually lost weight.

These experiments did not duplicate any actual known conditions in nature. Some of the constituents of ground waters have been used as solvents for silica before (Lovering, 1923). These experiments probably cannot duplicate natural conditions of time, and natural catalysts of clays. Further study of time relationships is being made.

Table I - Results of Solution Experiments

No.	Weight container, grams	Water, grams	Silicic acid, grams	Added reagent, grams	Weight geode fragment March 1, 1938	Weight geode fragment May 1, 1938	Weight change grams	Calcium in solution	Silica in solution
1	409.70	400	5.3000	$NaOH$ 21.6752	28.1400	28.1916	+0.0516	no trace	strong
2	413.90	400	5.0950	19.5732				no trace	strong
3	411.00	400		18.7532	28.0673	28.0688	+0.0005	no trace	strong
4	404.04	400		20.1632				no trace	strong
5	414.50	400	5.4290	$NaHCO_3$ 21.6125	24.2890	24.2966	+0.0076	no trace	strong
6	411.85	400	5.5432	21.0125				no trace	strong
7	414.17	400		19.6780	25.8955	25.8915	-0.0040	no trace	strong
8	296.00	400		20.0385				no trace	strong
9	414.50	400	5.1150	$CaCO_3$ 19.8580	21.7480	21.7400	+0.0080	trace	strong
10	409.56	400	5.1340	20.9580				trace	strong
11	410.80	400		19.5735	19.5430	19.5460	+0.0030	medium	strong
12	410.98	400		20.5751				medium	strong

Table I - Continued

No.	Weight container, grams	Water, grams	Silicic acid, grams	Added reagent, grams	Weight geode fragment March 1, 1938	Weight geode fragment May 1, 1938	Weight change grams	Calcium in solution	Silica in solution
				$Ca(OH)_2$					
13	410.50	400	5.2576	20.2080	32.3584	32.3590	+0.0006	strong	trace
14	411.00	400	5.3140	20.1324				strong	trace
15	411.90	400		20.9770	24.5845	24.6050	+0.0205	strong	trace
16	413.00	400		20.7400				strong	trace
				$CaCO_3$					
17	410.70	400	5.0080	20.5580	25.7102	25.7070	+0.0032	medium	strong
18	414.92	400	5.4430	21.4212				medium	strong
19	411.30	400		21.3370	27.1210	27.1180	-0.0030	trace	no trace
20	412.35	400		20.8980				trace	no trace
				MgO					
21	414.32	400	5.3174	10.1332	25.7500	25.7430	-0.0070	no trace	no trace
22	407.00	400	5.7264	9.8099				no trace	trace
23	412.20	400		10.6371	22.1328	22.1346	+0.0018	no trace	trace
24	410.75	400		10.1205				no trace	trace

Table I - Continued

No.	Weight container, grams	Water, grams	Silicic acid, grams	Added reagent, grams	Weight geode fragment March 1, 1938	Weight geode fragment May 1, 1938	Weight change, grams	Calcium in solution	Silica in solution
				*MgO NaHCO					
25	405.05	400	4.3482	*8.9952 10.1558	24.2928	24.3200	+0.0272	no trace	trace
26	397.00	400	5.2692	*9.1107 10.1318				no trace	trace
27	412.50	400		*9.9739 9.1440	21.2686	21.2890	+0.0294	no trace	trace
28	412.42	400		*8.8789 9.5520				no trace	no trace
29	410.50	400	11.0690		32.9184	23.8578	-0.0606	trace	trace
30	409.52	400	13.2904					no trace	trace
31	409.80	400			15.6098	15.5890	-0.0298	trace	trace
32	412.00	400						no trace	trace
				sodium silicate					
33	411.10	400		32.4445	14.9700	14.9815	+0.9115	no trace	strong
34	412.20	400		29.8400				no trace	strong
35	409.13	400		32.1842	14.1142	14.1175	+0.0033	no trace	strong
36	409.20	400		33.5130				no trace	strong

SUMMARY

Local concretions were observed in the field and collected for laboratory studies. A careful study of the literature in the college library has shown that while similar concretions have been observed elsewhere, there is no general agreement concerning their origins. It is evident that more work should be done.

Calcareous concretions were found to occur in soils and in unconsolidated sediments. In each case a source for lime may be found nearby. The occurrence of the concretions suggests relatively rapid precipitation and a relatively recent origin.

Iron sulphide concretions are found in shales near Manhattan and it seems probable that they were formed at nearly the same time that the sediments were deposited. Limonite concretions, those containing hydrous oxides of iron, are very common, although it seems that their origin is closely related to the weathering of the surrounding rock.

Concretions of celestite are exposed in fresh road cuts, but older exposures do not show celestite. Celestite is often classified as an insoluble mineral, but it dissolves appreciably in rainwater. Geodes of calcite are found in the cavities left by the celestite.

Siliceous concretions are very common in the Flint

Hills. Chert or flint nodules are present in limestone, and from the relation of chert to the limestone it is assumed that the age is nearly the same. Chalcedony found in the same limestones is, however, a much more recent deposit. Chalcedony probably deposits, as the original chert weathers away.

Certain quartz geodes containing calcite and chalcedony have apparently been formed from simple chalcedony concretions. The petrographic microscope shows quartz developing within the chalcedony. Some of the chalcedony nodules had formed around large calcite crystals which dissolved away later, leaving angular cavities. These cavities were lined with quartz crystals. A later generation of calcite was deposited upon the quartz crystals in some instances.

Some solution-deposition experiments were carried out. These were designed to show the relations between solutions saturated with silica and geode fragments, as compared with the relation of unsaturated solutions to geode fragments. Some rather interesting changes in weight were obtained, and chemical tests showed the presence of silica and calcite in solution. The following reagents were used in the solutions: sodium hydroxide, sodium bicarbonate, calcium carbonate, calcium hydroxide, calcium bicarbonate, magnesium oxide, sodium silicate, and silicic acid. The experiments indicate some solution and some deposition.

ACKNOWLEDGMENT

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PLATES

Explanation of Plate I

Figure 1. Diagram of a typical exposure of Cottonwood Limestone, showing the erosional terrace or table. Chert nodules (a) are present in beds within the limestone, and geodes (b) may be found in the soil above the limestone.

Plate I

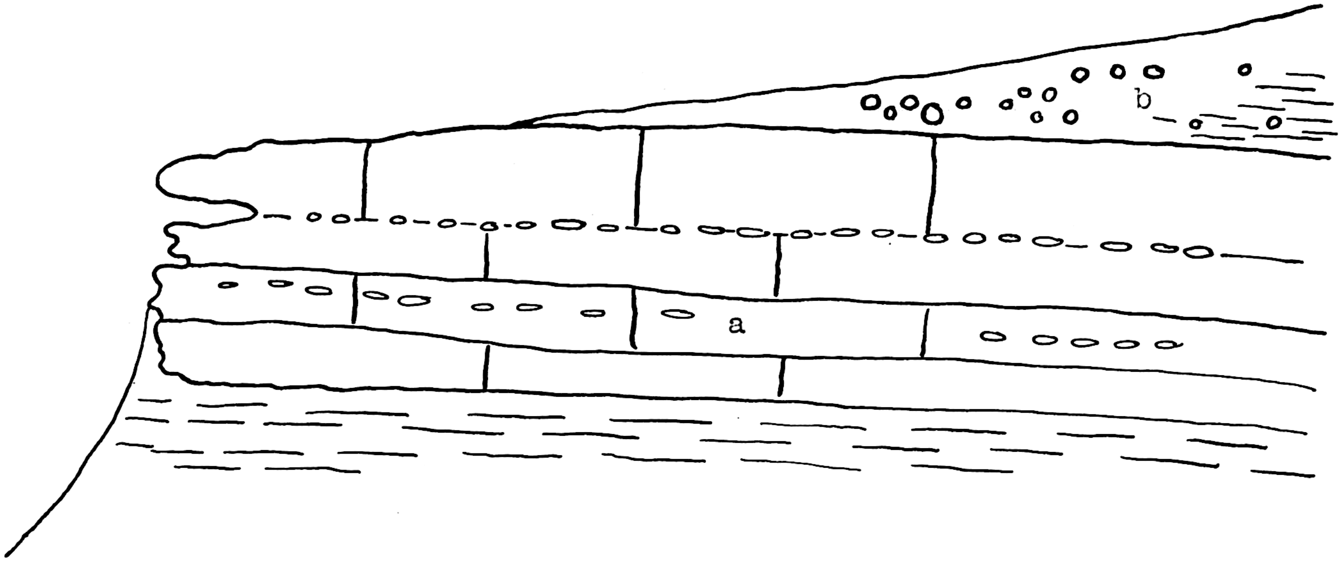


Figure 1

Explanation of Plate II

Figure 2. Section of a calcareous portion of the Elmdale Shale. Celestite nodules (a) are present a few feet from the weathered surface (b). Nearer the surface the celestite disappears and calcite geodes (c) appear.

Figure 3. Elmdale Shale, the same strata as in figure 2. An old soil (a) is buried under loess and a later soil (b) has developed. Celestite nodules (c) are still present at some distance from the surface. Calcite geodes (d) are close beneath the newly formed soil. Small geodes of quartz and chalcedony (e) are present in the old buried soil.

Plate II

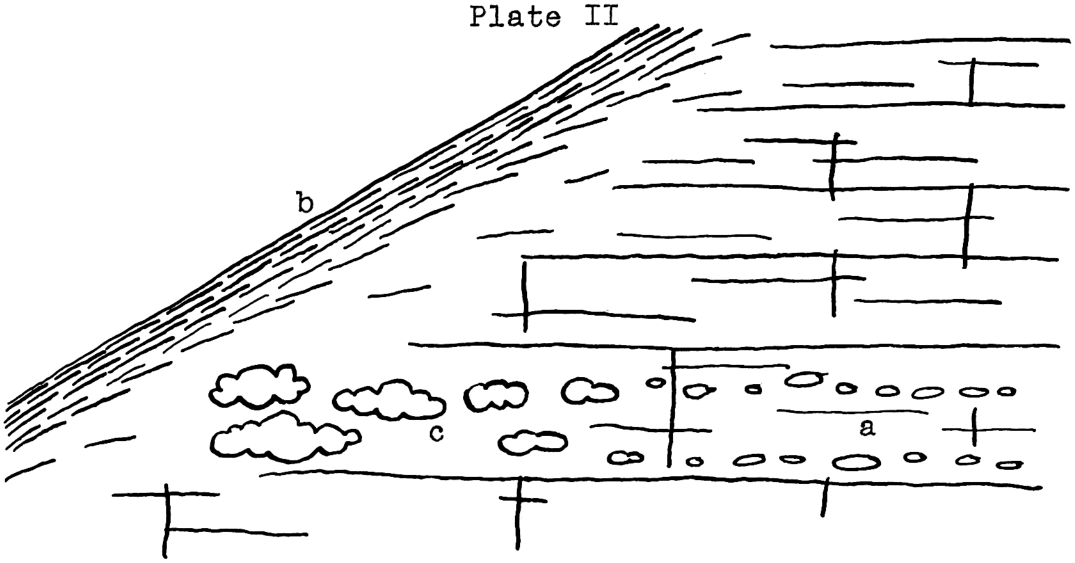


Figure 2

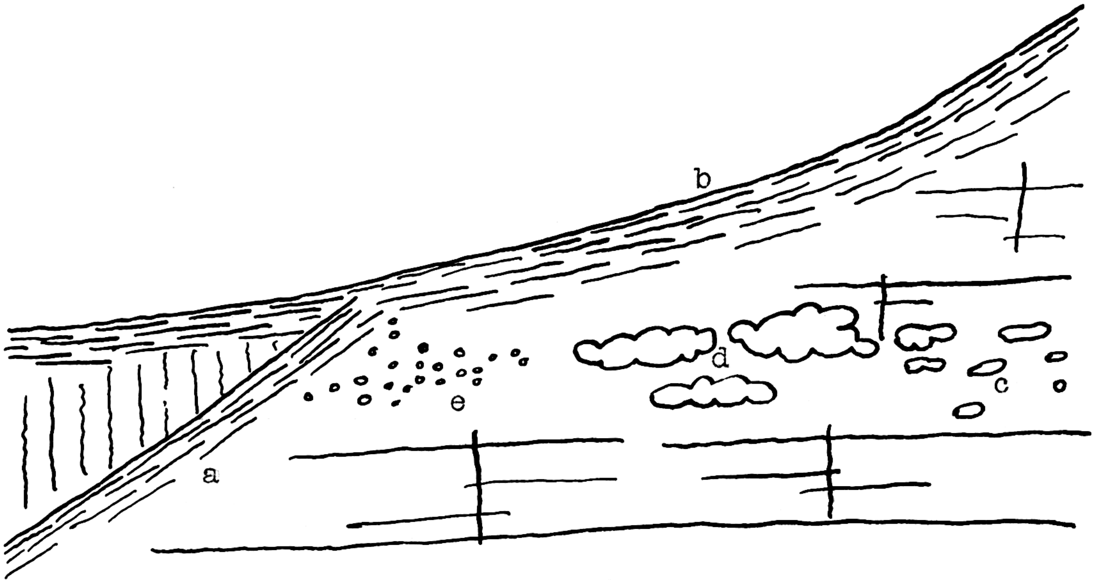


Figure 3

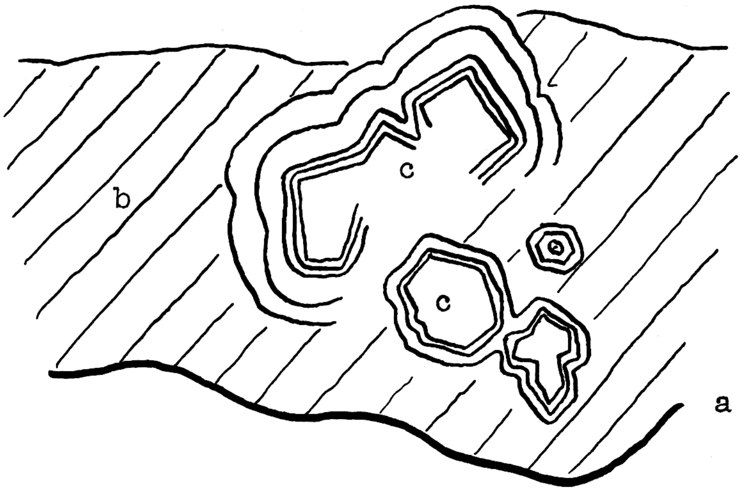
Explanation of Plate III

Figure 4. Portion of a geode wall (G1) magnified thirty-two times. The outer surface is marked by the heavy line (a). Vaguely banded or unbanded chalcedony is indicated by the diagonal lines (b). Quartz crystals (c) are surrounded by bands of chalcedony. The number of bands is related to the size of the quartz crystals.

Figure 5. Portion of geode wall (G6) magnified thirty-two times. Quartz (a) shows growth lines which are reflected in the chalcedony (b).

Figure 6. Thin section G11 magnified thirty-two times. Quartz (a) shows growth lines only in the portion which is surrounded by chalcedony (b).

Plate III



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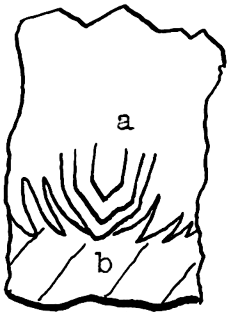

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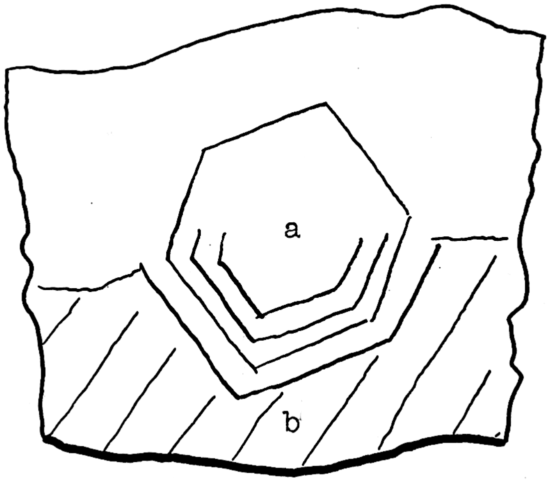


Figure 6

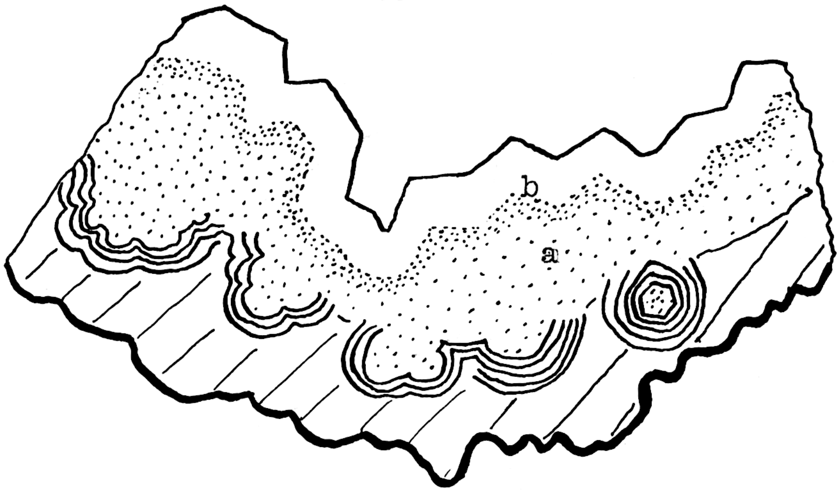
Explanation of Plate IV

Figure 7. A portion of a geode in slide G16 showing two generations of quartz. Etched and rough looking quartz (a) is covered over by more recent clear quartz (b).

Figure 8. Slide G17 shows quartz with a record of development. The crystal (a) shows a hexagonal section, half in chalcedony. Dark growth lines and new clear quartz show the record of growth.

Figure 9. Another portion of G17 shows three hexagonal sections along the line between chalcedony and clear quartz.

Plate IV



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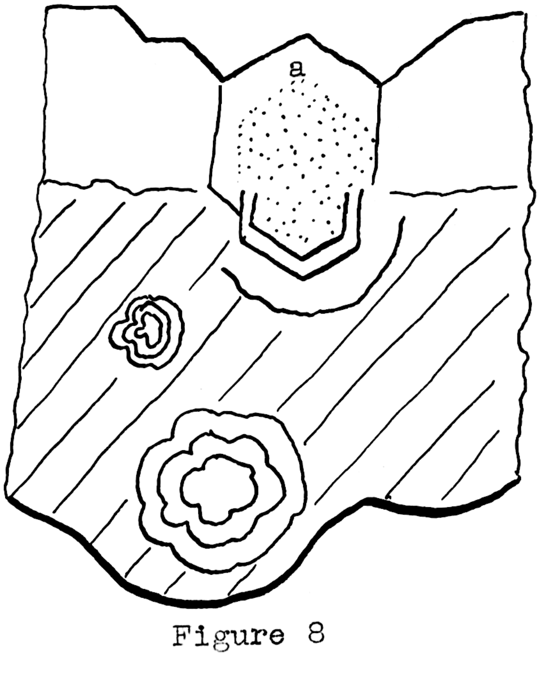

Figure 8

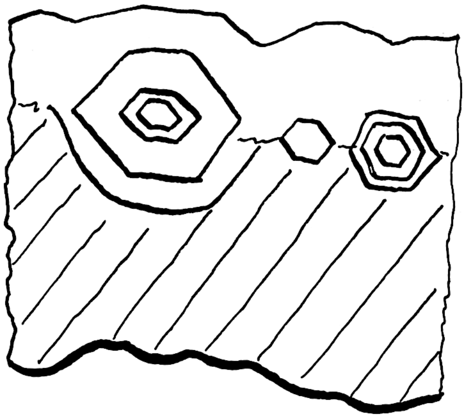

Figure 9

Explanation of Plate V

Figure 10. A portion of slide G21 enlarged thirty-two times. Two radial clusters of clear quartz are surrounded by banded chalcedony. The larger cluster (a) is surrounded by more bands of chalcedony than is the smaller cluster (b).

Figure 11. Slide G18 shows a radial cluster of quartz in chalcedony of a geode wall.

Plate V

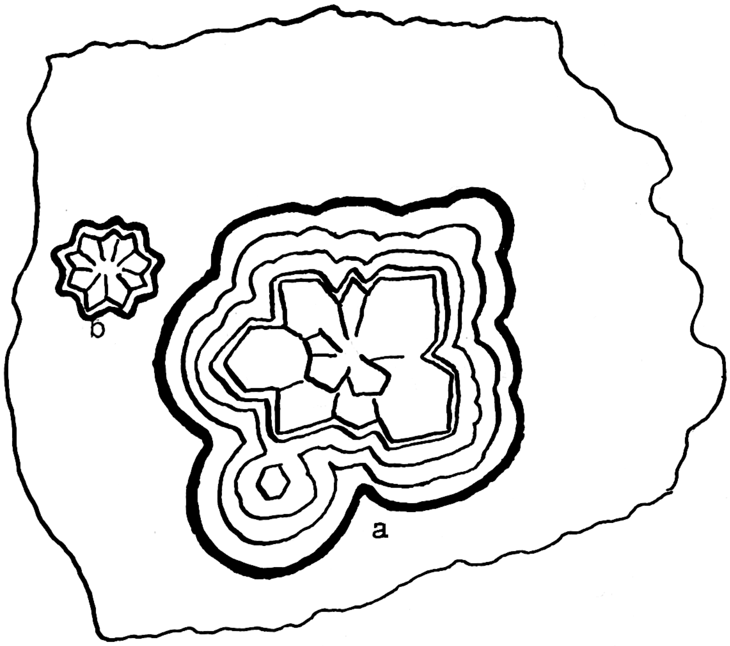

Figure 10

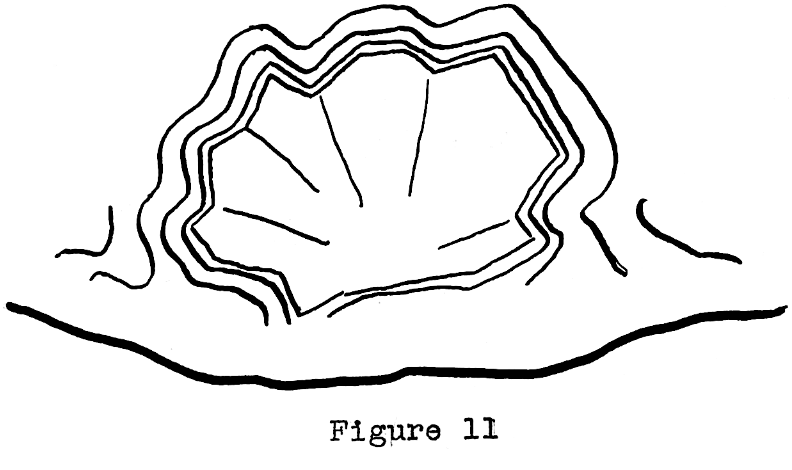

Figure 11

Explanation of Plate VI

Figure 12. Slide G45 shows chalcedony banded around a radial cluster of quartz crystals.

Figure 13. Slide G15 shows bands of chalcedony around a radial cluster of quartz. Bands farther from the quartz are interrupted or incomplete.

Plate VI

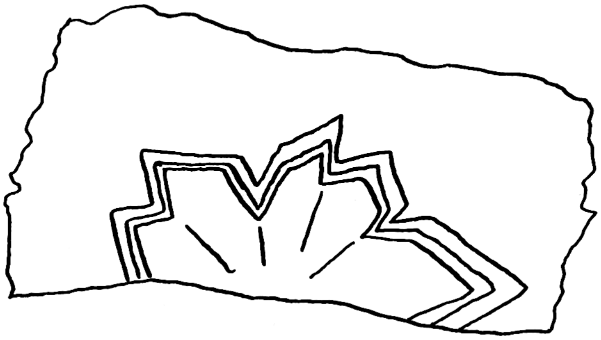

Figure 12

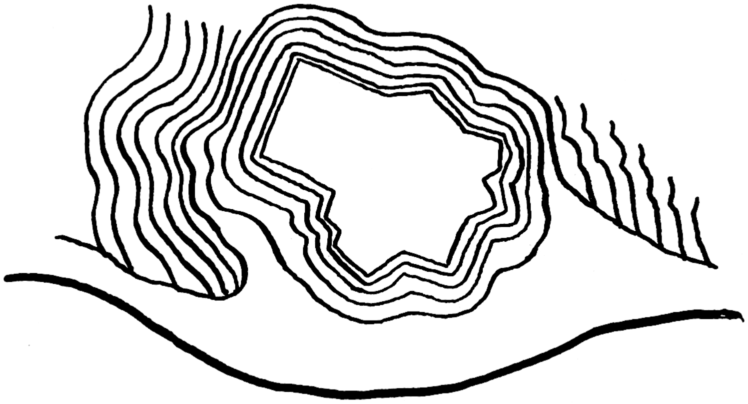

Figure 13

Explanation of Plate VII

Figure 14. Diagram of a concretion of chalcedony (a) deposited upon calcite (b). The chalcedony has started to recrystallize as quartz in one area (c).

Figure 15. The calcite of figure 14 has been dissolbed away, leaving an angular cavity (a). More chalcedony has been deposited (b). Quartz crystals are growing at various places (c).

Figure 16. The hollow concretion has become a geode. The central cavity is lined with quartz (a) and the chalcedony (b) is being recrystallized into quartz.

Figure 17. Quartz forms inside the geode (a) while chalcedony is added to the outside (b)

Plate VII

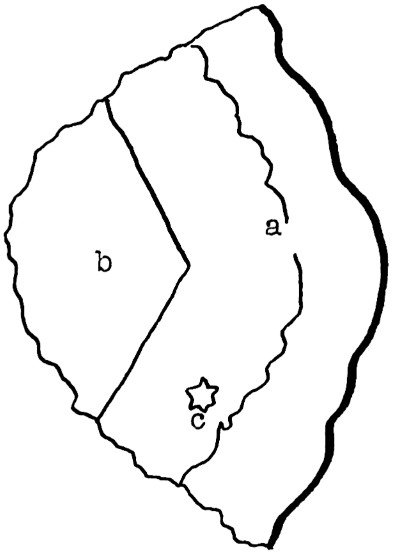

Figure 14

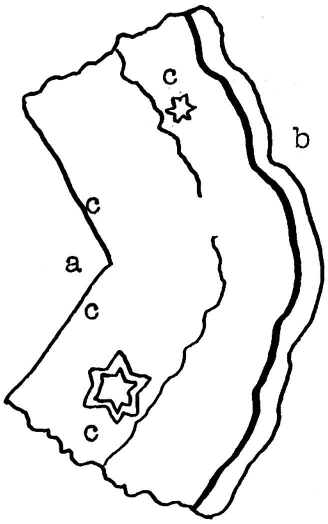

Figure 15

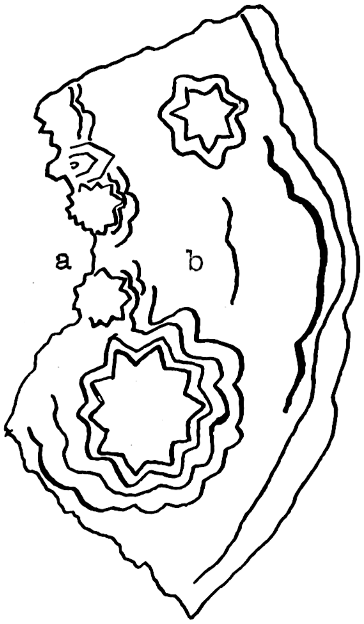

Figure 16

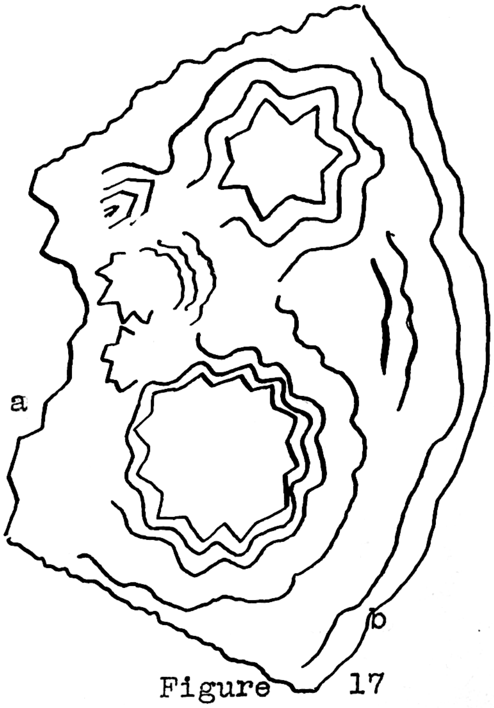

Figure 17

Explanation of Plate VIII

Figure 18. This is a photograph of a portion of slide G28; the magnification is about sixteen times. A radial cluster of quartz (at the right) is surrounded by chalcedony bands. The small dots are bubbles in the balsam.

Figure 19. This is a photograph of the same section as in figure 18. The nicols are crossed.

Plate VIII

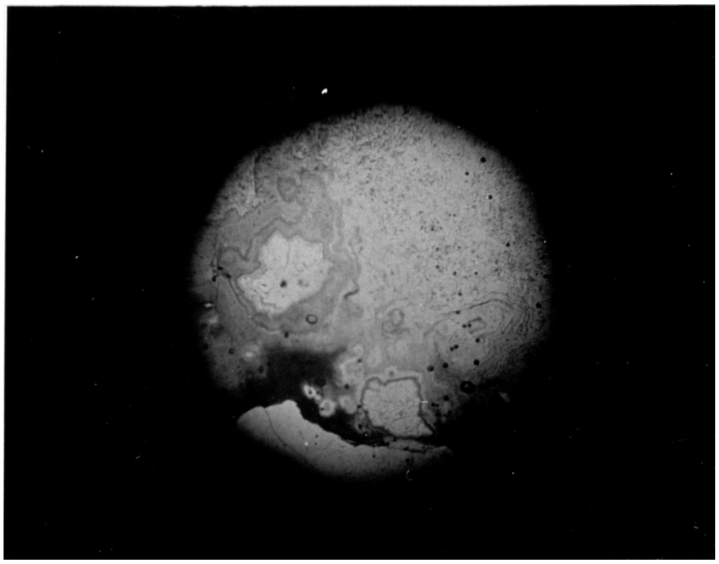

Figure 18

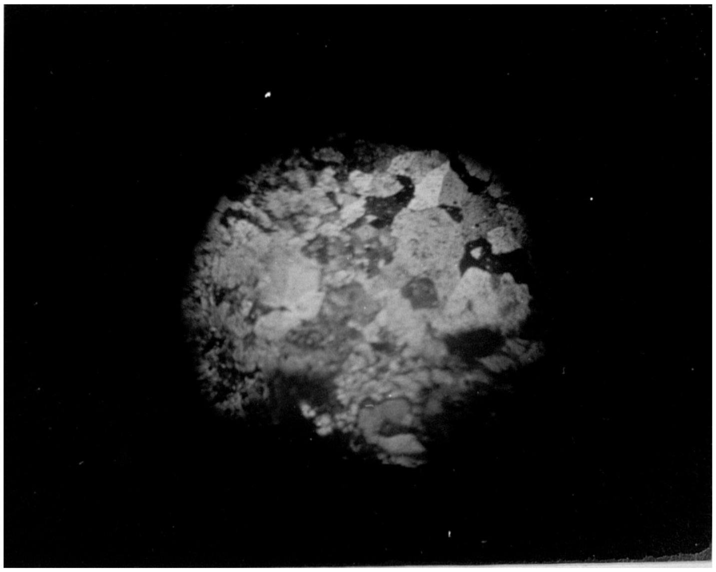

Figure 19

Explanation of Plate IX

Figure 20. Slide G1 shows quartz crystals surrounded by chalcedony bands (Fig. 1). The bubbles are outside the geode. The magnification is sixteen times.

Figure 21. Slide G21 shows various quartz-chalcedony relationships. The black and the gray portions are chalcedony, and the clear, unbanded portions are quartz. The magnification is sixteen times.

Plate IX

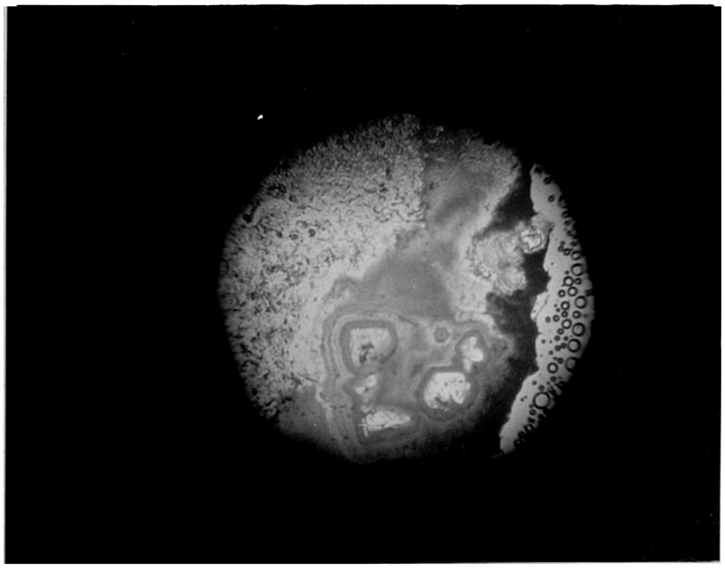

Figure 20

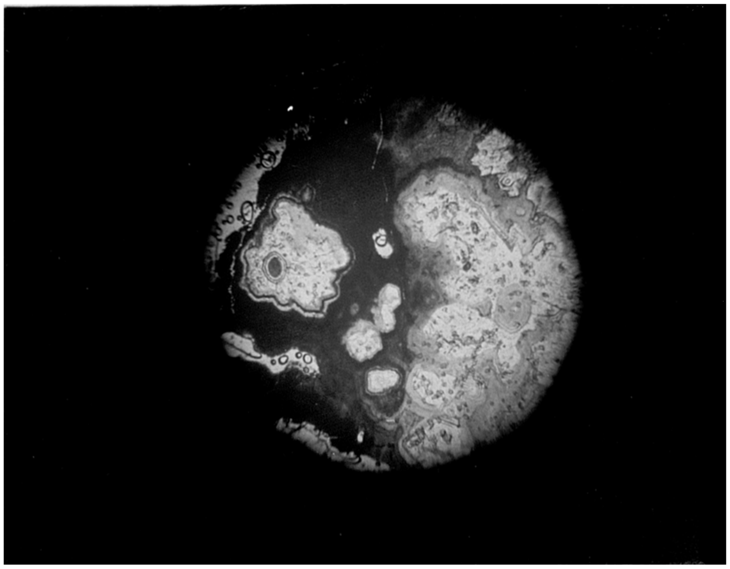

Figure 21