

BULLETIN

OF THE

NATIONAL SPELEOLOGICAL SOCIETY

VOLUME TWENTY-FOUR

PART TWO

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SYMPOSIUM ON CAVE MINERALOGY

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JULY 1962

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Published twice a year; Editor: William E. Davies, 125 W. Greenway Blvd., Falls Church, Va.; Associate Editors: Nancy G. Rogers, George W. Moore, Mrs. William W. Youdon, Harry M. Meyer, Jr.; Assistant Editors: Thomas C. Barr, Jr., Richard Anderson, Kenneth Christiansen, Rane Curl. Inquiries relating to the publishing of manuscripts in the BULLETIN should be addressed to the editor.

Office Address:

THE NATIONAL SPELEOLOGICAL SOCIETY
2318 N. KENMORE ST.
ARLINGTON 1, VIRGINIA

Subscription rate in effect January 1, 1962: \$4.00.

Stalactite

EDITOR'S NOTE—This article is a translation of an important work in the history of speleology. It was originally published in Copenhagen in 1655 as part of *Museum Wormanum* by the Danish naturalist Olao Worm, 1588-1654, and includes the first use of the word *stalactite* as well as a reasonable account of stalactite formation. These excerpts were translated from the original Latin by Bro. G. Nicholas, F.S.C.

For the class of small stones called *Bergdrab* in Norwegian, we propose the name STALACTITE, a stone usually ash colored tending toward yellow, which assumes various shapes according to its origin, its mode of deposition, and the structure to which it adheres. It is formed by deposition from water which has rock-forming properties because it carries within itself finely divided mineral matter. As the water flows either through channels in the earth, or drips down from above, or precipitates on the banks of streams, it correspondingly produces various shapes. Dripping down from a high crack, it adheres where it can in the shape of a cone, and in this manner it congeals into the same shape as water flowing from the crack in the cold of winter would ordinarily freeze. It may be found in various places in Denmark, Norway, Germany, Iceland, Italy; and it has various shapes and characteristics.

I have several of those specimens which belong to the ICICLE class. My first one is porous, light in weight, and built up from smaller icicles and droplets which, like small entwining worms, cling to the stone and form branches. Each tiny icicle, which is white tending toward yellow, no matter how fragile and twisted it may be, actually has an internal cavity which extends to its open end.

I have an icicle-shaped STALACTITE three inches long from Norway closely resembling a true icicle, except that small branches resembling leaves have developed on the sides in two places where droplets of water squeezed out; it barely exceeds a swan's quill in thickness, white in color with a roughly crystalline appearance; when the shaft is turned, the grains sparkle like well compacted salt.

I also have another STALACTITE from Norway, solidified drop by drop, with round, oblong, or pear-shaped beads making up a homogeneous mass, so that it is not too far-fetched to call it a CLUSTER OF GRAPES. It is white, shiny, and composed of small smooth beads of equal size although differing in shape.

From France I have received another specimen which is shiny, white, of the consistency of sugar, found in an underground cave called *La Cava Guttiere*, two leagues from the city of Tours. Note that those who wish to enter this cave must have torches to furnish light; it is cold in this cave in the middle of summer while it is warm in the winter as is usual with underground caves. Here the water, as it seeps through the pores of the ceiling in the form of vapor, gradually produces stone which acquires a luster on account of the purity of the rock-forming fluid.

Water also solidifies in the hot springs of Iceland, and it is converted to a crusted STALACTITE. Last year a young Iceland native, Trebonius Jonas, sent me a specimen of this sort, giving me this information in a letter on its origin:

I am sending a certain stone-like material transmuted from clay or wood (so it is believed) which can now be seen in the hot spring referred to in the preface of Saxo's book, which is locally called GEYSER (rushing furiously) because the heat engendered there causes the water to rush furiously up into the sky. The highly distinguished and illustrious Bishop Brynolphus, D.D., recently had some wool placed in this spring as an experiment, because he considered that this substance is the exact opposite of stone, since it is so flexible. Whatever meta-

HISTORIA
RERUM RARIORUM,

Tam Naturalium, quam Artificialium, tam Domesticarum,
quam Exoticarum, quæ Hafniæ Danorum in
ædibus Authoris servantur.

Adornata ab

OLAO WORM, MED. DOCT.

&c, in Regiâ Hafniensi Academiâ, olim
Professore publico.

Variis & accuratis Iconibus illustrata.



LUGDUNI BATAVORUM,

Apud IOHANNEM ELSEVIRIUM, Acad. Typograph.

MDCLXX.

morphosis is to be expected there, time and experience will reveal. This was what he wrote.

The specimen which I have here is almost square, the same in length as in width, three inches, ash gray, rough surfaced, hardened slowly by accretion, sandy, quite like wine tartar. This makes it evident that it is not composed of transmuted clay or wood but is solidified from a salt such as tartar, borne in this hot spring water but now separated from it. Whence I am persuaded that this hot spring does not turn anything into stone but coats it with a crust such as stone or tartar. I believe that this will happen to the wool that was placed in it as an experiment, for the crusts amply demonstrate the

source from which our stone was solidified. The hot spring from which these objects arise is said to be located near Skalholt, in the so called Haukedalur or the valley of hawks.

STALAGMITE appears to be of the same nature and substance as Stalactite. But it differs in shape, at least, as it is always solidified as globes. A specimen was brought to me from Karlsbad, hardened from rounded or globular drops of water, which have coagulated into gypsum rock of the same shape, and have a shiny color approaching black. The separate globes exactly resemble peas in size and color, which explains why they are commonly called KARL'S PEAS for they are often found at Karlsbad. The whole stone is like a mass of coarse fish roe; a good many peas are actually contained in this large mass, with each one enclosed in its own honeycomb cell or compartment from which they are easily extracted.

LARGE GLOBULES, of which I have three types, may also be noted here. Some of them are lustrous perfect globes, and these may be either single, or sometimes paired, or in three's or four's, composed of a white gypsum-like material. Wherever these large types are solidified from ash-colored marble, they are in pairs.

Likewise certain other marble stones, but having a brown color, are fused together in two's or three's. Book 24, chapter 27 of Imperatus attempts to investigate the reason for the globular shape and maintains that this is caused by rotation within the water which often makes angular objects become rounded, or by the motion of the water itself. In hot subterranean regions, those that have easy access, where the ores are of sulfur or alumina, globules of this type are found, either singly or fused together, solidified from liquids or from subterranean vapors. But I believe that the place into which the subterranean rock-forming liquid drips has a great deal to do with this question. For if it drips into a channel of round cross section, whether it is a single channel or is joined to another, globular stones are formed, especially in the case of those composed of marble.

Introduction to the Symposium on Cave Mineralogy

by William B. White

The environment of the surface of the earth is perpetually frustrating to the mineralogist, the oceanographer, and the geochemist. Ambient conditions of temperature and pressure result in such slow reaction rates that reactions will not come to equilibrium in any reasonable length of time. A cave forms an ideal natural laboratory for studying low temperature reactions since underground the temperature and pressures remain constant for long periods of time. The study of cave mineralogy, therefore, is likely to be rewarding not only in terms of useful information about the cave minerals themselves but also because the information may be applied to other areas such as the chemistry of weathering and chemical oceanography.

To bring various workers in this field together, a symposium on cave mineralogy was held in December, 1960, at the New York meeting of the American Association for the Advancement of Science. The symposium was jointly sponsored by the National Speleological Society, the Geological Society of America, and Section E of the AAAS. The individual papers presented at this symposium and the discussion which followed them are published in this Bulletin.

Aragonite, according to chemical data, is only stable at 25°C. above a pressure of 3000 atmospheres. Yet aragonite is perhaps the third most common cave mineral. Curl has proposed a new approach to this metastability problem by suggesting that the known promoters of aragonite crystal growth work through a nonequilibrium mechanism of preferential poisoning of growth sites (perhaps screw dislocations) on calcite nuclei while perhaps promoting the formation of metastable aragonite nuclei.

The problem of rate of calcite crystal growth in the cavern environment came under considerable attack. Bassett and Bassett examined the growth of a monocrystalline hexagonal stalactite and postulate

the necessary conditions for growth of such deposits. Moore examined the question of rate of stalactite growth in general. The more rapid rate of growth of calcite along its c-axis results in crystals with their c-axis pointed in the direction of growth outgrowing crystals with less favorable orientations resulting in a final crystal with its domains oriented perpendicular to the growth surface. Slow rates of growth at low supersaturation results in the formation of few nuclei and promotes the development of monocrystals.

Geochemical stability relationships were applied to the problem of the fracture filling and mineralization of Wind Cave by White and Deike. Evidence was presented that the minerals in this cave may have been deposited from hot solutions. The Wind Cave minerals may form an interesting transition group from normal cold ground water mineralization and hydrothermal mineralization (The caves of the Iowa-Illinois-Wisconsin Lead-zinc district for example).

Since the symposium was limited in time and its scope was limited almost entirely to the anhydrous carbonate minerals, it may be appropriate here to point out a number of other cave mineral problems that await solution.

The basic problem of determining the number and distribution of cave minerals has hardly been begun. The few caves that have been studied intensely have been found to contain entirely unsuspected minerals. Until this work is done, one will not know the bulk composition of the mineralizing solutions one is attempting to interpret.

The moonmilk problem is being attacked with considerable vigor, especially by French speleologists who are advocating a biochemical origin. It does not seem wise to abandon traditional thermodynamics until all avenues of attack have proved hopeless. Much of the thermochemical data for the system $\text{CaO} - \text{MgO} - \text{H}_2\text{O} - \text{CO}_2$ is already in existence

in an extensive literature on carbonates. There remains but to make the necessary calculations to apply this data to caves.

The sulfate minerals were hardly mentioned during the symposium and yet they are the second commonest group of cave minerals and are under considerable study. Knowledge of the system CaSO_4 — MgSO_4 — Na_2SO_4 — H_2O would allow one to explore the implications of many sulfate hydrate minerals which exist in caves but which quickly decompose when brought into the surface atmosphere. The possibility exists, for example, that degree of hydration of the sulfate minerals measured along the radius of large speleothems might be a "geo-hygrometer" recording the relative humidity of ancient cave atmospheres.

Black manganese deposits are common in many caves and are commonly referred to as "manganese dioxide". The few specimens that have been identified are not manganese oxides at all but rather heavy metal manganates. It seems from this scanty evidence that cave manganese deposits may act as scavengers for metal cations, concentrating them in far higher proportions than would ever be found in cave waters. This close similarity in behavior between cave deposits and the manganese nodules of the ocean floor can scarcely be overlooked.

Two other groups of minerals deserve attention. The origin of the nitrate minerals

is still not settled to everyone's satisfaction. Several recent detailed studies have shown extremely complex suites of phosphate minerals to occur in caves where organic material reacts with the wall rock. However, there is as of yet little data on the stability relations of these minerals.

The petrography of cave travertine deposits is a non-chemical problem of importance. The study of the texture and orientation of the crystal layers in cave deposits by thin-section techniques could potentially provide information on the earlier cave history. Study of cave chemical sediments could then be combined with study of cave clastic sediments to provide additional material for interpretation of the sequence of cavern development.

G. W. Moore, introducing the 1959 symposium on the origin of limestone caves, was able to point to large areas of general agreement contrasted with a few points in decided dispute. Speleogenesis is an old and well-established subject. The study of cave mineralogy is in its infancy. The detailed theoretical treatments, inevitable mothers of dispute, have not even been developed.

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The Aragonite-Calcite Problem

by Rane L. Curl

ABSTRACT—Aragonite is about 16 percent more soluble than calcite and hence unstable with respect to it. However, both are stable with respect to the ions in solution during precipitations when the supersaturation with respect to calcite exceeds the solubility of aragonite. Under this condition, the relative rates of crystal nucleation and crystal growth determine which polymorph will dominate. In the literature may be found a great deal of information on how temperature, trace impurities and rate of precipitation promote one or the other polymorph, but there is essentially no information available on the mechanisms of nucleation and growth. Most conclusions are inferential.

It is proposed here that aragonite occurs much more frequently than is usually believed and that while aragonite is never stable with respect to calcite, unless the latter is only present as minute crystals, various factors can produce an apparent or kinetic stability which is responsible for the precipitation and preservation of aragonite crystals. The calcite — aragonite problem is discussed in the light of the Theory of Crystal growth. It is suggested that the effects of foreign ions and molecules are due to interactions on both aragonite and calcite with the origin and spreading of the crystal growth steps. While growth layers and spirals arising from screw dislocation in the crystal lattices have never been observed on calcite or aragonite, they are probably responsible for the growth of these materials as they are for other crystals. In this view strontium, magnesium and other ions and molecules may induce the precipitation of aragonite or calcite either by providing isomorphous nuclei, by absorbing on either calcite or aragonite growth steps and modifying relative growth rates, or by causing lattice distortions after adsorption which lead to the creation of the dislocations which aid growth. Temperature modifies the rates of all these mechanisms and, in addition, probably plays some primary role involving solvation of the surface or motion of dislocations.

Further understanding of the aragonite-calcite problem now rests upon study of the fundamental mechanisms of nucleation and growth of these polymorphs in the absence or presence of foreign substances. Further studies of what substances are able to promote aragonite or calcite precipitation under different conditions will not be nearly as useful as would be kinetic studies on single crystals of the two polymorphs under carefully controlled conditions of temperature, supersaturation, and impurity ion type and concentration.

INTRODUCTION

Crystalline calcium carbonate occurs in nature as calcite (rhombohedral), aragonite (orthorhombic) and vaterite (hexagonal). It has long been recognized that this is the order of decreasing stability, and so the question of the natural occurrence of aragonite and vaterite has received considerable attention. The relative abundance of the three polymorphs, calcite common, aragonite rare but widespread and vaterite very rare, reflects the basic differences in their thermodynamic properties. The second most common polymorph, aragonite, is the primary

subject of this paper. It is its occurrence in caves that has prompted some of the work on aragonite because, in this environment, it is found precipitating simultaneously with calcite under apparently identical conditions. The same problem, however, is also found in living organisms where some species of molluscs selectively deposit calcite, others aragonite, and still others both polymorphs.

Aragonite is about 16 percent more soluble than calcite in any solvent. Only great differences in crystal size are known to be able to change this relative solubility under

normal conditions. Whenever aragonite is precipitating from solution, the solution must be also supersaturated with respect to calcite. Consequently, the aragonite-calcite problem requires consideration of issues concerning both polymorphs, for we may ask "What inhibits the precipitation of calcite?" as well as "What promotes the precipitation of aragonite?"

It has been found that certain additives and certain conditions of temperature can have a pronounced effect on whether aragonite or calcite appear in laboratory preparations. Certain effects are very striking. Two of these are the small range of temperature over which *in vitro* precipitation can go from almost completely calcite to almost completely aragonite, and the effect of magnesium ion whose carbonate is not isomorphous with aragonite and is not very soluble in the aragonite lattice but which seems to promote the appearance of aragonite. The natural occurrence of aragonite has been variously attributed to the effects, separately or in unison, of temperature, strontium, magnesium or sulfate ions, organic molecules in solution, and stabilization of the aragonite lattice by assorted means. On the other hand, the picture to be offered in this paper will emphasize the competition between the rate mechanisms of nucleation, crystal growth, and dissolution for the two polymorphs rather than seeking a unique cause or determining factor.

A body of knowledge basic to understanding the problem is all the physical and chemical properties of the polymorphs, although we do not know, in most cases, how this knowledge applies. The reader is referred to Graf (1955, 1960) for this background. A review of carbonate chemistry and calcite polymorphs is given by Mellor (1923). The material on aragonite-calcite relations is largely an uncritical but thorough account of the literature from 1788 to 1922 with a large account of the observations which had been made on comparative *in vitro* precipitations. From the standpoint of geochemistry Doelter (1912), Rankama and Sahama (1950) and Abelson (1959) should be consulted. A natural occurrence of vaterite, plus a review, is described by

McConnell (1960). Whenever aragonite is discussed, strontium comes up also as its carbonate (strontianite) is isomorphous with aragonite. Strontium distribution in rocks, minerals and other deposits is covered by Turekian and Kulp (1956) and Gundlach (1959) in addition to the above references on geochemistry.

In this paper the biological origins of aragonite will not be discussed despite their interest and pertinence. Some workers feel that biological activity is the key to occurrences of aragonite under cave conditions. If this is so, the conclusion will revolutionize the problem. In any event, the almost totally inorganic view taken here does not exclude biological agencies, as even these must act through the mechanisms of crystal growth and alter the calcite-aragonite competition. The considerable literature on biological origins can be reached through Stolkowski (1951), Pobeguín (1954a), Revelle and Fairbridge (1957), Sogannaes (1960) and Turekian and Armstrong (1960).

A considerable number of references will be given here, but this is not intended to be an exhaustive bibliography of the subject. Recent work will be emphasized, though this may usually be a key to the earlier work.

An attempt was made in 1916 by Johnston, Merwin and Williamson to "give a coherent critical statement of the facts and discuss the deductions which, in the light of present knowledge, may legitimately be drawn from them". The present work is much in the same spirit. Furthermore it arrives at the same conclusions when they say, "The form which actually precipitates is, in the absence of nuclei isomorphous with any of these forms, determined presumably by whichever nucleus first separates; but as to which this is likely to be under given conditions, nothing definite can be stated at the present time . . . if we suppose that all of the types of nuclei are present simultaneously in the liquid, the question as to which appears is a question of the relative probability of the configurations of the several nuclei, and hence is not likely to be elucidated until more is known about the real structure, and mode of growth, of crystals". These authors

recognized the distinction between apparent factors which cause or promote the appearance of aragonite and the mechanisms by which these factors must act.

In the following sections the identification, natural occurrence, recent work on the subject, stability relations and growth phenomena will be discussed. An attempt will then be made to summarize what we know now and some ways to proceed toward greater understanding.

IDENTIFICATION

A note is included here about the identification of calcite, aragonite and vaterite because of difficulties which must be avoided. The most direct method is inspection of the crystal form of the massive material or fragments. Errors can sometimes be made in ordinary inspection because of the possibility of pseudomorphism (for example, Andrews and Scheller (1942)). However, calcite fractures into rhombs and aragonite into rather irregular fragments. Optical methods require laboratory equipment but allow positive identification if the material is in a suitable form. Identification by X-ray diffraction is certainly the most definite and has come into standard use. A source of error in even the X-ray diffraction method can occur in the preparation of the sample by grinding, as this is able to convert calcite to aragonite (Burn, 1956; Dacheille, 1959). Infra-red adsorption spectra have also been used. Pobeguín (1954b) summarizes these physical methods.

The staining methods are summarized by Friedman (1959). They are based on the small difference of solubility of aragonite and calcite and hence the alkalinity of the solution in contact with them. Consequently, an "aragonite" test is obtained with aragonite, vaterite, hydrates of calcium carbonate, very finely divided calcite or amorphous calcium carbonate and other inorganic and organic compounds which give an alkaline reaction, or mixtures of these with calcite. When working with new materials which give an aragonite test, an X-ray confirmation should be obtained. The Wisconsin Geological Survey found, upon checking with X-ray, that all their "aragonite" specimens were pseudomorphs of calcite after aragonite (per. comm.).

OCCURRENCE

Reports of the occurrence of aragonite are scattered and, in many cases, missing for areas in which the author personally knows the mineral to occur, and yet when it is reported it is often found in relative abundance. There are two main reasons for this state of affairs: aragonite is not a mineral of economic significance and it is difficult to identify in the field. The early work on aragonite suffers from the lack of positive identification methods and only recently has X-ray diffraction been widely adopted.

Aragonite is, of course, of world-wide distribution. It is named after the locale in Spain where it was first identified as a separate mineral. While this report does not give world-wide coverage, noteworthy references are: France, Gèze (1957); Czechoslovakia, Kuscer et al (1959) and Kaspar (1957); Russia, Tatarskii (1955); and Japan, Kitano (1955).

In 1960 a letter was written to each of the geological surveys or equivalent bureau in each of the states and the provinces of Canada inquiring about references to aragonite in each area. The answers plus a separate search produced the following summary of the literature on aragonite occurrences. No effort was made to verify the reports, so it is possible that some field identifications were incorrect. Aragonite from recent shells of organisms is not included. The author acknowledges the kind assistance of the many geological surveys and other individuals who provided this information.

No reports were found on aragonite occurring in any of the following: Arkansas, Delaware, Florida, Idaho, Illinois, Maine, Massachusetts, Michigan, Minnesota, Mississippi, Montana, New Hampshire, North Carolina, Oklahoma, Rhode Island, South Carolina, Tennessee, Vermont, Wisconsin, Alberta, Manitoba, New Brunswick, Newfoundland, Prince Edward, Saskatchewan, Yukon and Northwest Territories; only by personal communication were Alaska, Georgia, Kentucky, Maryland, North Dakota, Ohio and Oregon not included among the above.

Typical references emphasizing cave occurrences of aragonite were found for the following states and provinces: Alabama,

Pallister (1955), Armstrong (1958); Arizona, Galbraith (1947), Moore (1956); California, Murdock (1948), Logan (1951); Colorado, Moore (1956), Johnson (1957); Connecticut, Sohon (1951); Hawaii, Stearns (1939); Indiana, Erd and Greenberg (1960); Iowa, Bain (1899), Peck (1959); Kansas, Swineford and Frye (1955); Louisiana, Hanna and Wolf (1938); Missouri, Bretz (1956); White and Stellmack (1959); Nebraska, Schramm (1943); Nevada, Moore (1956); New Jersey, Wilkerson (1959), Mason (1960); New Mexico, Black (1953). Moore (1956), Northrop (1959); New York, Whitlock (1903, 1910); Pennsylvania, White and Ellisher (1958); South Dakota, Tullis and Gries (1938), Moore (1956); Texas, Hanna (1938); Utah, Eardley (1938), Moore (1956); Virginia, Henderson (1949), Foster (1950), Murray (1951); Washington, Shannon (1923); West Virginia, White (1957); Wyoming, Allen and Day (1935), Goldring (1941), Osterwald and Osterwald (1952); Canadian Provinces, Quebec, Poitevin, (1918), Johnston (1915).

Some of the best cave displays of the acicular form are known from California, Colorado, Missouri, South Dakota, Texas and Virginia. However, it would seem that, if the acicular form is not present, aragonite is not identified from that site. An exception which suggests what might be the real situation is reported by White (1959) who found most of the aragonite in Carroll Cave, Missouri, to be present in massive (but microcrystalline) forms. It is the author's opinion that aragonite is much more common than presently known — perhaps universal in caves. Certainly the present extent of study of aragonite in caves comes no where near supplying the information to confirm or refute this suggestion.

RECENT LABORATORY WORK

It is beyond the scope of the present discussion to review critically the whole of the work that has been done on the laboratory preparation of the calcium carbonate polymorphs. This has also been beyond the scope of other workers, which leaves a vast body of experiments only evaluated by the authors and mentioned by a few subsequent writers. Mellor (1923) names some three

dozen such experimental efforts, devoting only a sentence or two to each. With the wide variety of experimental plans used, sources of materials, methods of identification of the products, techniques of conducting the experiments, and different purposes, it is no wonder that previous experiments are seldom repeated. While it would seem desirable to eventually attempt the total evaluation of all the earlier work, it is not likely that this will be done soon, if ever. There is a lesson in this for new experimenters: that their work is likely to join the vast body of unevaluated, and perhaps unevaluatable, work, unless the experiment provides a definitive answer to a particular question. Ever since aragonite and calcite were recognized as polymorphs, attempts have been made to explain why particular conditions lead to one or the other. The majority of this work has been concerned with demonstrating conditions (temperature, pressure, foreign ions, nuclei, rate of precipitation, etc.) that would consistently lead to aragonite, calcite, or mixtures. From such demonstrations, explanations have been deduced, usually along the lines that one condition or another "promotes" or "determines" the occurrence of aragonite or, more rarely, calcite. The other approach to an explanation — seeking the causes in the mechanisms of precipitation of one phase or the other — has received relatively little attention.

An eclectic, if sketchy review of the subject up to 1922 has been presented by Mellor (1923). Somewhat earlier reviews by Linch and Leitmeier are in Doelter (1912). By 1922 it was recognized that aragonite was probably always unstable with respect to calcite at atmospheric pressure, and the following factors tended to promote the appearance of aragonite whether by slow or rapid precipitation: aragonite nuclei, isomorphous nuclei (strontium, barium, lead carbonates), magnesium ion, sulfate ion, high pH, high temperature (over 30°C) and the presence of urea, while rapid cooling or rapid filtration prevented the reversion of aragonite to calcite. Some contradictions appear in the earlier work. It may be that this is, in part, due to the difficulty of distinguishing which form is present and

the possibility that inappropriate techniques were used. Also, not only the conditions of precipitation but also those of subsequent digestion played a role which may have obscured the former. Almost without exception the work reviewed by Mellor was concerned with observations of the agencies responsible.

It was pointed out by Johnston, et al (1916) that, when the solubility product for calcite is exceeded, calcite will begin to precipitate if nuclei of calcite or an isomorphous material is present. Otherwise, the solution may be increased in concentration until the solubility products of all unstable species (aragonite, vaterite, hydrates) are exceeded under which circumstances the form to appear depends on which nuclei forms first or is present. If all are present, the growth mechanisms then determine the polymorph to predominate. The importance of particle size was also pointed out and bicarbonate ion was suggested as a "promoter" of calcite relative to aragonite. The essential ingredients of a modern theory had been stated: the need for supersaturation with respect to both aragonite and calcite; the subsequent importance of the mode of growth of the two phases; the role of nuclei; and the probable importance of other ions during the growth process to direct the precipitation to either aragonite or calcite.

In a long overlooked paper, Saylor (1928) draws upon the analogous situation of habit modification of crystals by the presence of impurities during precipitation, to suggest an explanation. Although he believed that aragonite could be thermodynamically stabilized with respect to calcite by ions in solid solution (see Stability), he did observe that any theory to account for the appearance of metastable forms must embody the idea that calcite crystals were prevented forcibly from growing by preferential adsorption of impurities. Saylor suggests urea, acetate ion, bicarbonate ion, "the high temperature form of water" and chitin (or other substances of biological origin) act to inhibit the growth of calcite and thereby give the advantage to aragonite. Examples of other similar polymorphic stabilizations are given to support this argument.

Faivre (1946, 1950) discussed the agency of temperature in the artificial precipitation of vaterite, aragonite, and calcite, hypothesizing that vaterite always precipitates first and transforms to aragonite or calcite via solution and recrystallization. This idea has not been confirmed. Brooks, et al (1950) found unstable species to be promoted by increasing precipitation rate or by addition of Calgon or magnesium ion. They prepared calcite, aragonite, vaterite, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ and noted that the growth of certain nuclei can be inhibited by additives. The rapid laboratory precipitation was also studied by Dekeyser and Degueudre (1950), who demonstrated again the importance of pH and temperature. Some stress was laid on the order of succession, vaterite-aragonite-calcite, as was often done in earlier work.

Besides reviewing the subject through 1950, Stolkowski (1951) proposed that carbonic anhydrase played an essential role in "orienting" the precipitation of aragonite by molluscs. A similar role was assigned to conchioline by Roche (1951).

The normal instability of aragonite with respect to calcite in the earth's crust was finally quantitatively determined by Jamieson (1953). He consequently repeats the proposal that the conditions of "metastable" precipitation must be considered, rather than those of equilibrium, for both *in-vivo* and *in vitro* occurrences. Later work by McDonald (1956) and Clark (1957) confirmed Jamieson's results.

A very extensive account of the appearance and source of aragonite and calcite precipitated both by organisms and inorganically was prepared by Pobeguín (1954a). The comparative roles in organic, organic associated and inorganic precipitation of pH, temperature, foreign ions (discounting any importance of magnesium or strontium in the environment of organisms as being determining factors), colloid promoters, and enzymes and the rapidity of precipitation, and hence supersaturation, as causes of aragonite formation. In subsequent notes (1955, 1957), Pobeguín emphasized again the importance of supersaturation via rapid precipitation in organisms and caves.

In an independent study, Murray (1957) also precipitated calcium carbonate under conditions designed to simulate the cave environment. In addition, he added magnesium, lead, strontium ions and aragonite or calcite nuclei and concluded that variations in the mineral content of water evaporating in caves explains the growth of the polymorphs in proximity. The quite striking aragonite-promoting influence of magnesium ion, when present in large concentrations, was again demonstrated.

Agents of aragonite precipitation *in vitro* are given emphasis again by Zeller and Wray (1956) who believed that the "impurity content of the crystals" is the immediate factor influencing the form of calcium carbonate precipitates; foreign ions trapped in the nucleus may influence the crystal form and time, temperature pH, etc. may all influence the extent to which such "determining" ions are trapped. Except for a seeming implication that oriented overgrowth is essential for aragonite precipitation, these authors do not suggest a mechanism for the action of impurities. A similar study with similar results was performed by Harada and Masaru (1957). Temperature is also emphasized by Moore (1956) in an attempt to use the appearance of aragonite in caves to estimate paleotemperatures. His map of aragonite occurrences versus temperature for the western United States is thought-provoking though exceptions have been noted. His discussion of the subject suggests that the actual role of temperature may be quite obscure, perhaps through its effects on other physical, chemical and biological factors.

Wray and Daniels (1957) extended and refined the notions of Zeller and Wray on the important effect of impurity ions. However, their most striking result is the reconfirmation of the long known narrow range of temperature in which artificial precipitations produce nearly 100 percent aragonite or 100 percent calcite. This is so striking that one wishes that the precipitation could be carried out with *absolutely pure* reagents to determine if the effect is via impurities or is unique to temperature. That strontium *per se* does not determine aragonite, at least in biological preparation, was shown

by Banks and Odum (1957) who forced chickens to make eggs with up to 25 percent strontianite. The remainder was calcite.

Lippman (1960) suggests an explanation for the action of magnesium ion in apparently promoting aragonite, at least in slow artificial precipitation. In order to grow water-free aragonite crystals, the hydrated calcium ion in solution must lose its water of hydration, which involves considerable energy. Magnesium ion is even more strongly hydrated and therefore, since Mg^{2+} is preferentially adsorbed on the calcite surface, calcite growth is inhibited by the necessity of releasing this bound water of hydration.

Most of the observations noted above provide more questions than they answer. The few attempts at suggesting mechanisms touch on only narrow aspects of the overall problem and are indeed not even confirmed. On the whole, the phenomena of aragonite precipitation which have been described, commented upon, and redescribed are wide open to research on causes and mechanisms. We may say only that we know the following: Calcium carbonate nuclei promote the same polymorph by epitaxy or oriented overgrowth; super-saturation with respect to *both* calcite and aragonite is a necessary condition for aragonite precipitation; the inhibition of calcite growth is consequently a necessary feature of aragonite precipitation; and that a whole assortment of additional factors seem to be important in the competition between aragonite and calcite nucleation and growth. We do *not* know specifically how any of these factors act in this competition, although suggestions have been made and surmises follow from considerations of crystal nucleation and growth.

STABILITY

If aragonite exists for long periods in contact with a solution in equilibrium with calcite, it is obvious that the aragonite is "stable," in some sense, with respect to calcite. The words "stabilized with respect to" have been used in connection with the effects of many agents on the relative precipitation of aragonite or calcite. It is important therefore that agreement be reached as to the meaning of these words, and appropriate modifiers be used if it is apparent

that more than one effect is being described.

The most generally accepted meaning of the word *stable*, when applied to minerals, and especially to polymorphs, refers to the *thermodynamic stability of the massive form of the crystal*. In exact terms, we would speak of the free energy difference between calcium carbonate molecules in the calcite lattice and in the aragonite lattice. If the *free energy* is greater in aragonite than calcite, aragonite is unstable with respect to calcite. *This is a property of the molecules in the crystal lattices, and the composition of the contacting solution is irrelevant*. The result of many years of research has pretty conclusively established this. Early measurements were made, and reviewed, by Bäckström (1921) though the best modern values were obtained by Jamieson (1953) who established that, at standard conditions, the free energy difference between calcite and aragonite is 272.5 ± 3 cal/mole. MacDonald (1956) suggested, by thermodynamic calculations, that if strontium carbonate were to stabilize aragonite by solid solution (dilution of the calcium carbonate in the solid), concentrations of the order of 30 percent would be required — a magnitude never found in nature and rarely reached in the laboratory. More direct evidence on this point is furnished by Mondange-Duffy (1960) who studied the high temperature monotropic transformation of aragonite to calcite at about 400°C, for aragonite precipitated with different impurity ions. The aragonite always transformed to calcite, so no impurity could stabilize (thermodynamically!) aragonite at these temperatures, but the rate and activation energy of the transformation was strongly affected by foreign ions, some having the opposite effect of others. We may also conclude from this work that aragonite never undergoes a solid state transition to calcite at ordinary temperatures and pressures. This transformation is much too slow; any observed recrystallization from one polymorph to the other must have taken place through the agency of the solvent.

Now that the concept of thermodynamic stabilization of aragonite with respect to calcite in nature has been shown to be unimportant, two situations which may be un-

sidered as exceptions must be noted. The first is the effect of a size difference between particles of calcite or aragonite. The solubility of a substance depends upon the particle size, or rather the curvature of the surface, which is great for small particles, because the non-isotropic surface molecular forces produce a more significant increase in internal lattice stresses on small crystals with relatively greater surface to volume ratios. Assuming a surface energy of 100 ergs/cm² for the calcite-water interface (A measured value is not available; see Gilman (1960).), the critical size for a calcite crystal to have the same equilibrium concentration as massive aragonite is about 130Å. Such particles, although not visible in a light microscope, would be expected to result from rapid precipitations or grinding of calcite. It is known that excessive solubilities can result in such cases. Aragonite would therefore be stable with respect to such finally divided calcite. Likewise, if there are no larger calcite nuclei present, the aragonite would be *metastable* with respect to massive calcite as no nuclei could form at the concentration in equilibrium with aragonite. Such nuclei would first have to pass through states of smaller size, which would be unstable with respect to the solute. The electric double layer on calcium carbonate surfaces probably modifies these stability relations (Vasátko and Kohn, 1955).

Jamieson's value for the free energy difference between aragonite and calcite at 20°C and 1 atm (272.5 cal/mole) is equivalent to a solubility ratio of the two polymorphs of 1.16 at the same (though arbitrary, if not too low) carbon dioxide pressure. More recently, Weyl (1959) obtained a ratio of 1.14 from careful solubility measurements. Thus, aragonite and calcite have very close solubilities so that it takes very little shift in the concentration of a solution with respect to calcium and bicarbonate ion (at a given CO₂ pressure) to have neither, only calcite, or calcite and aragonite stable *with respect to the ions in solution* (though, of course, not stable with respect to each other). A small shift in carbon dioxide pressure can also make this change. When precipitation of aragonite is occurring under these conditions, it is usually spoken of as

metastable precipitation, which it is if the reference is the stable calcite. However, if the reference is the supersaturated ions, it is not improper to observe that both polymorphs are then *stable* with respect to the ions available for their precipitation.

Aragonite now occurs in nature under conditions which do not seem to be covered by the above cases of thermodynamic stability or metastability. We must then conclude that, in such cases, the aragonite is transforming to calcite, except at such a slow rate as to be unobservable. Such limitations on the rate of transformation might be called *kinetic stability*, and the state the new factors preserve, *metastability*. Dry aragonite appears to be kinetically metastable at temperatures below about 300°C (Mondange-Dufy, 1960). Therefore the transformation at ordinary temperatures must occur by solution and reprecipitation on suitable calcite nuclei. If the solution rate of the aragonite or the growth rate of the calcite is suppressed by the presence of other ions or impurities, the aragonite could survive for considerable periods of time. Such inhibition of the surface processes of solution or deposition are well known. A particularly striking example for *calcite* is the inhibiting effect of certain ions on the formation of the bicarbonate to the extent of an apparent change in the equilibrium concentration, demonstrated by Terjesen, Erga, Thorsen and Ve (1961). They found the following order of decreasing effectiveness as inhibitors for calcite solution: Pb^{2+} , La^{3+} , Y^{3+} , Sc^{3+} , Cd^{3+} , Cd^{2+} , Cu^{2+} , Au^{3+} , Zn^{2+} , Ge^{4+} , Mn^{2+} , Ni^{2+} , Ba^{2+} , Mg^{2+} , and Co^{2+} . This is the same order as found by Gorlich (1958) for the absorbing ability of calcite. There was a clear parallelism between increasing effectiveness as inhibitor and decreasing solubility of the carbonate. These experiments were not tried with aragonite. Wray and Daniels (1957) found they could "stabilize" precipitated aragonite by the addition of strontium ion. Similar results might be expected with the ions tested by Terjesen, et al. Parallel effects are associated with growth of the calcite or aragonite phase where trace concentrations of foreign ions and molecules can strongly affect the relative rates of crystal growth. If these impurities inhibit calcite

during growth, an apparent kinetic stability of aragonite is exhibited. The effects of impurities during growth from a solution supersaturated with respect to both come under the subject of growth kinetics and the idea of relative "stability" cannot be properly applied.

GROWTH

Johnston, et al, (1916) suggested that we wouldn't get anywhere with this problem until more is known about the mode of growth of crystals. We still know nothing to speak of about the mode of growth of calcium carbonate crystals, but quite a bit has been learned since 1916 about the general picture of crystal growth. Therefore, it is opportune to see if any of this knowledge helps in understanding the calcite polymorph problem. The following sketch of crystal growth is based primarily on Doremus, Roberts and Turnbull (1958). A bibliography on the subject through 1957 has been prepared by Bennett (1958). The reader would also find Verma (1953), Dekeyser and Amelinckx (1956) and Van Bueren (1960) quite informative.

The fact that crystals have flat faces means that they must grow by the spreading of layers over the faces. Otherwise new molecules would place themselves anywhere and the resulting growth would be essentially shapeless. This means that each growing layer is bounded by a peripheral step, and it is only at this step that molecules can be added to the crystal lattice from the adjacent liquid phase. When an individual layer, perhaps only a few molecules thick, has spread over the face on which it is growing to the edges of that face, no sites remain for further growth unless there is a mechanism for creating new layers. Two proposals have been made for the generating of new growth layers; one is nucleation of a new layer due to high supersaturation in the liquid phase. This undoubtedly occurs but is unlikely at low supersaturations. The second is that certain imperfections in the crystal lattice, called *screw dislocations* intersect with a surface to produce a permanent source of growth steps. Figures 1-6 illustrate these two mechanisms for the creation of growth layers. In Figure 1 is shown simple, two-dimensional growth due to surface nu-

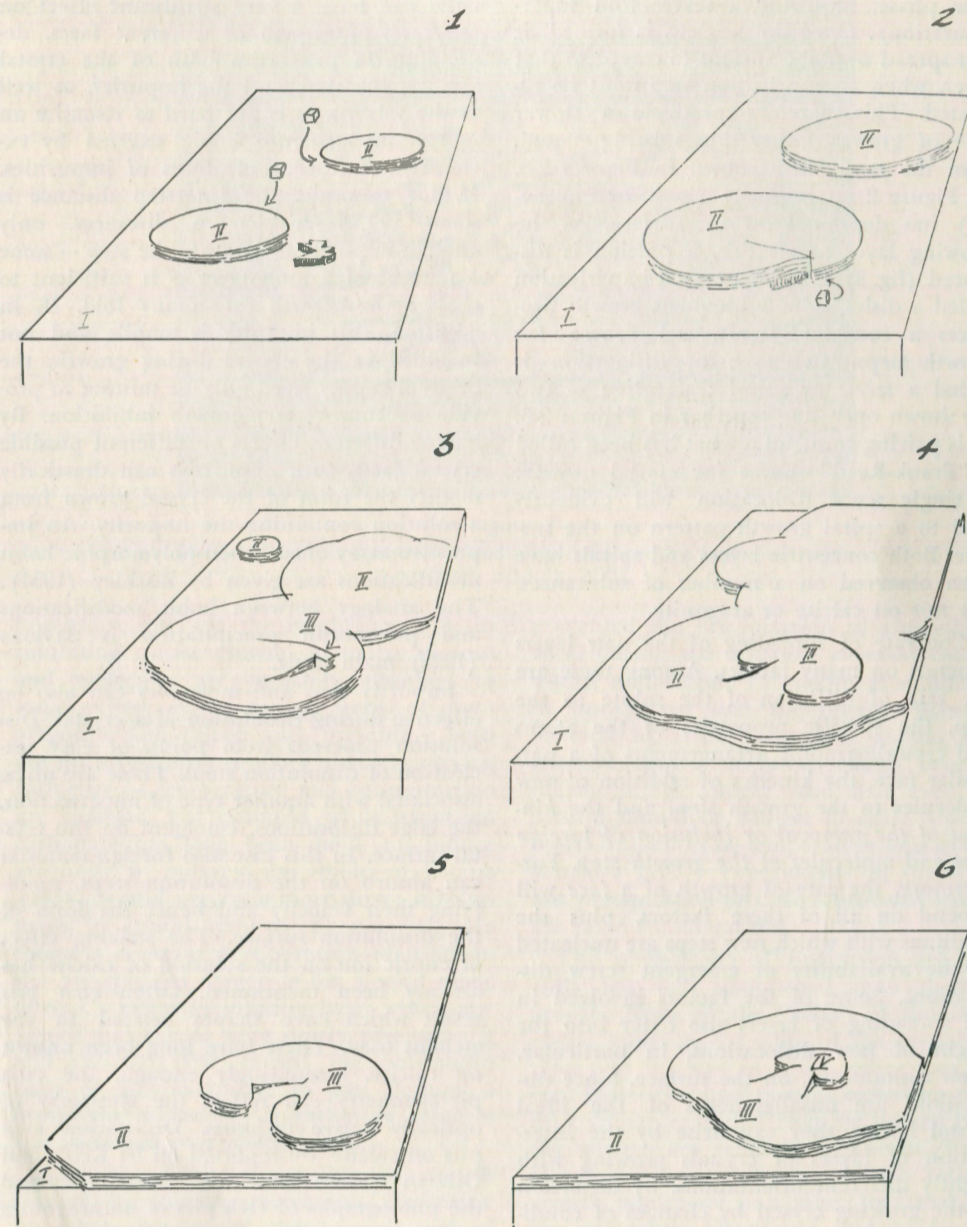


Figure 1-6
Possible mechanism of creation of successive growth layer from paired screw dislocations arising from the interaction of a growth layer and an adsorbed impurity.

cleation (this is much like nucleation of a new phase, requiring a several-fold supersaturation). Once the nucleus is formed, it can spread over the surface to complete that layer, when the nucleation step must be repeated. This therefore produces a slower rate of growth, other things being equal, than the mechanism shown in Figures 2-6. In Figure 2 an impurity (ionic or molecular) has deposited on the surface. As the growing layer covers this, a portion is displaced (fig. 3) to form a crystal imperfection called a dislocation. Subsequent growth produces a continually renewed source for growth steps. This type of dislocation is called a *screw* or *spiral dislocation* — two are shown operating together in Figures 2-6. This pairing constitutes what has been called a "Frank-Read" source for crystal growth. A single screw dislocation will evidently lead to a spiral growth pattern on the surface. Both concentric layers and spirals have been observed on a number of substances, but not on calcite or aragonite.

The rate of spreading of the new layers depends on many factors. Among these are the rate of diffusion of the solute to the step, the specific properties of the atoms and crystallographic arrangements of a particular face, the kinetics of addition of new molecules to the growth step, and the *kinetics of the removal or inclusion of foreign ions and molecules at the growth step*. Furthermore, the rate of growth of a face will depend on all of these factors, plus the readiness with which new steps are nucleated or the availability of emergent screw dislocations. Some of the factors involved in the spreading of layers also enter into the origin of new dislocations, in particular, screw dislocations, on the surface. Since dislocations are misalignments of the ideal crystal lattice, they can arise by the intersection of layers or crystals growing with slightly different orientations, by distortion of the growing crystal by changes of conditions of growth, and by the inclusion of foreign ions and other impurities in the crystal. Anderson (1956) has shown how screw dislocations can arise in the nucleus of crystals by misoriented growth, and Williams (1957) by local deformation of larger crystals.

It is easy to see that foreign ions and molecules can have a very significant effect on the rates of growth of different faces, depending on properties both of the crystal surface, the step, and the impurity, as well as the solvent. It is not hard to visualize an important influence being exerted by extremely small concentrations of impurities. If, for example, the interstep distance is some 100 layer-thickness distances, only enough impurity to saturate the step — some 1 percent of a monolayer — is sufficient to change the growth rate many fold. If, in addition, this impurity is mobile and not included in the crystal during growth, the original supply need only be minute to provide continuing step-growth inhibition. By having different effects on different possible crystal faces, such impurities can drastically modify the form of the crystal grown from a solution containing the impurity. An impressive array of such non-polymorphic habit modifications are given by Buckley (1951). The analogy between habit modifications and polymorph precipitation is Saylor's (1928) main topic.

Impurity ions and molecules can also be effective during dissolution of a crystal. Dissolution proceeds from points of easy nucleation of dissolution steps. These are often associated with another type of imperfection, the edge dislocations, emergent on the crystal surface. In this case also foreign material can absorb on the dissolution steps, modifying their velocity and hence the form of the dissolution surface. The striking effect of cupric ion on the solution of calcite has already been mentioned. Often *etch pits* result which have shapes related to the etchant used. These have long been known on calcite. Interestingly enough, the etch pit symmetry can reflect the symmetry of optically active etchants. Dislocation etch pits on calcite are reported on by Keith and Gilman (1960), and the author obtained the photographs of etch pits of an aragonite needle, from Titus Canyon Cave, Calif., shown in Figure 7.

In considering the impurities which may be involved in step-growth rate modification, the solvent itself should not be overlooked. Lippman (1960) has already suggested that water of hydration may play an

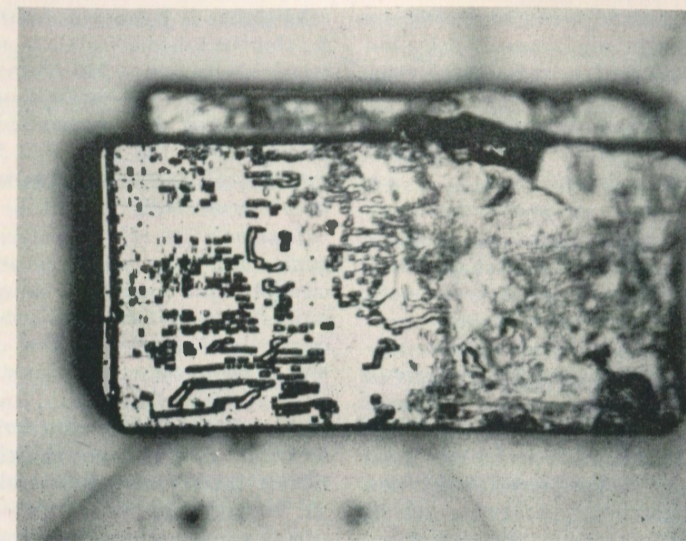


Figure 7
Etched pits on aragonite. Needle tip produced by treatment with carbonic acid (x 250).

important role, via the magnesium ion, in inhibiting calcite growth. Actually, all ions and molecules are probably adsorbed to some extent on the growth steps of *both* aragonite and calcite and, presuming both are nucleated, may produce a widely varying influence as temperature and concentration are changed. For example, while strontium carbonate has long been held to induce aragonite by epitaxy, the results of Kitano (1958) would suggest a more direct involvement in crystal growth phenomena. He found a constant Sr/Ca ration of 0.003 in the precipitated aragonite for a wide range of Sr/Ca ratios in solution from which aragonite and calcite were slowly precipitating and also that Sr^{2+} caused the polymorph ratio of the precipitate to pass through a *maximum* as the Sr/Ca ration in solution was increased over about 0.005.

Aragonite is also susceptible to growth control by foreign molecules. Hexameta-phosphate suppressed the precipitation of aragonite in addition to changing the morphology of calcite precipitation (Buehrer and Reitemeier, 1940), while Williams and Ruehrwein (1957) report that sodium polymethacrylate and the ammonia adduct of isobutylene maleic anhydride copolymer

prevented the precipitation of aragonite at 90°C during the reaction between calcium nitrate and sodium carbonate. It should not be unexpected that the organic materials secreted by living organisms should have selective control to some extent over the polymorph to appear, and that even this control should be subject to other superimposed influences of temperature and solutes. Buzagh's (1957) experiments on the rhythmic precipitation of CaCO_3 , probably involve the same considerations.

The phenomena of nucleation are presently less well understood than those of growth. None of the "rules" of the larger crystal apply at the scale of the crystal nucleus and the way in which other ions, solvent molecules, and foreign molecules enter into, or are excluded from or diffuse from, the nucleus are generally unknown. Suffice to say that nuclei, having a high ratio of growth points per unit mass (or area), being inherently disordered and readily including foreign ions and molecules, are probably quite strongly influenced in their stability (with respect to size) and rate of growth by impurities, the solvent, temperature, and mode of aggregation. This point is suggested by Wray and Daniels (1957),

although they probably overemphasize the role of strontium in nucleation. Nucleation by epitaxy or oriented overgrowth of polymorphic crystal species is discussed by Kleber and Verworner (1959). It should be noted that crystals need not be isomorphous for epitaxial growth to occur.

To summarize, we can say that all chemical species present during precipitation of calcite or aragonite, the primary ions, foreign ions, solvent molecules, organic molecules, etc., can adsorb at the growth steps of both calcite and aragonite and either slow down the spreading of these layers or be responsible for the creation of additional sources of growth steps; and that these impurities can interact and change roles on different faces or in the presence of different ionic environments. Likewise, all of these effects can enter into the critical nucleation stages which, though of humble beginnings, subsequently control the species which will grow. In this view the problem of the origin of calcite or aragonite in any precipitation can be considered as a competition between nucleation and growth for the two polymorphs. Whichever one can accomplish nucleation sooner and grow more rapidly will dominate. About all the observation made on the subject so far tells us are the agents which might be important in this competition. The mode of their action is still, on the whole, completely unstudied.

In the above treatment, it has been assumed that the solution is supersaturated with respect to both calcite and aragonite. If the solution is only supersaturated with respect to calcite naturally only calcite, and no aragonite, can appear. This is the case when massive aragonite is recrystallizing via solution to massive calcite. However, it is the author's belief that in all *in vitro* and probably in most *in vivo* precipitations the solution is supersaturated. Whether this is the case in slow mineral precipitations should be tested. Obviously, if aragonite does occur, the solution is supersaturated with respect to both and then the issues of growth competition are all important.

SUMMARY, POSSIBILITIES AND PROBLEMS

There are so many factors involved in the competitive precipitation of aragonite and

calcite that it is not yet possible to suggest a coherent scheme for their separate or cooperative influence. However, in the following paragraphs the attempt is made to outline some of the essential features of the problem with the hope that future specific studies will confirm, refute, or redirect the points made here.

Supersaturation, with respect to both aragonite and calcite, is necessary for the nucleation and growth of aragonite. Supersaturation is affected by temperature, rate of supply of solution, rate of evaporation or loss of carbon dioxide from solution, initial concentration of reactants, and rate of precipitation. While supersaturation is a necessary condition, it is not sufficient and other factors must enter. It would be useful if the actual saturation condition of the solution in contact with undisturbed speleothems of aragonite and calcite could be determined accurately.

Temperature can have secondary effects by increasing or decreasing the availability of other ions and metabolic products of organisms or by changing the rates of reactions and diffusion. However, a primary role in the competition between aragonite and calcite seems likely. Experiments should be performed in the complete absence of impurity ions and with controlled foreign ion concentrations. If a primary role occurs, it may be through growth inhibiting changes of the water-surface interaction on aragonite or calcite with change in temperature; via mechanisms of nuclei formation involving any of the polymorphs and hydrates of calcium carbonate; or by an influence on the perfection of the nuclei formed at high supersaturation due to a temperature dependency of the creation or mobility of dislocations in the nuclei. These or other mechanisms could function to inhibit or accelerate either aragonite or calcite nucleation and growth. Too little is known now to explain the temperature phenomenon.

Strontium ion (barium, lead) can provide its carbonate or other salt as a nuclei upon which aragonite will grow selectively, if present in high enough concentration to precipitate under the conditions (natural or experimental). It may also inhibit the

growth steps of either, though probably calcite more strongly, as it is "soluble" in the aragonite lattice, even at concentrations too low to precipitate. Likewise its adsorption on aragonite surfaces appears to kinetically stabilize them, by interfering with the spreading of dissolution steps, against recrystallization to calcite. These and other ions can also introduce distortions into the crystal from which the screw-dislocation growth centers can originate. This author believes that the commonly found higher natural concentrations of strontium in aragonite rather than calcite reflect a strontium partition coefficient favorable to the former. However, the common presence of strontium in aragonite for this reason, also makes it available for its other roles during conditions of dissolution. This may account in part for the preservation of some fossil aragonite corals studied by Siegel (1960). These mechanisms have been essentially unstudied. Oriented overgrowth of aragonite on strontium minerals should be tested as well as the quantitative effects on the growth and solution kinetics of both aragonite and calcite.

Magnesium ion appears to cause aragonite to be the preferred polymorph under most conditions of precipitation. As its carbonate is not likely to nucleate aragonite in preference to calcite, the primary effect must be during growth. The higher concentrations taken up by calcite reflect higher surface concentrations during growth which might be expected to inhibit calcite growth layers from spreading. Interaction with the solvent (water) has also been suggested as a mode of inhibiting calcite growth. It is also possible that, even though less soluble in the aragonite lattice, what does enter distorts the lattice and causes a higher rate of creation of growth promoting dislocations. Again, kinetic data with both are needed.

Sulfate ion has been implicated by some authors, but its effects are apparently not pronounced. It would be necessary to disentangle its possible roles as a precipitator of alkali earth sulfates, as a growth inhibitor or as a source of lattice distortions leading to growth sources. Other anions (CO_3^{2-} , Ac^- , $(\text{PO}_3)_6^{4-}$, HCO_3^{1-} , etc.) are also effective agents in the nucleation-growth

competition according to various authors.

Organic solutes or crystals may act in a similar fashion to ionic materials. They may provide surfaces for oriented overgrowth to nucleate either polymorph; inhibit growth steps on either to different degrees; or chelate ions or modify their effects on nucleation and growth or dissolution. Urea has been suggested as a calcite inhibitor; certain polyelectrolytes as aragonite inhibitors; conchioline as an aragonite orientor. None of these have received kinetic study. The organic materials present in actual natural waters consist of organic molecules from the soil and from organisms which could play diverse, and weather, temperature, etc., dependent, roles depending on how they interact with the growth processes. No natural or artificial aragonite has been tested for trace quantities (ppm) of organic compounds included in its lattice; such materials need to be tested for their growth orienting or kinetic effects. Likewise, the solutions from which aragonite or calcite are precipitating have not been analyzed by organic trace methods.

It is difficult to be more specific than this about the actual mechanisms of influence of each of the conditions or agents mentioned. In most cases the answer might be either acceleration of growth of one form or inhibition of the other; at least the existing work does not always distinguish between these possibilities. Although inhibition is more common, acceleration has also been observed. What is needed are quantitative measurements of the rate of growth of crystals under carefully controlled conditions of temperature, supersaturation, and impurity ion or organic molecule type and concentration present. In addition, studies of the oriented overgrowth of single crystals on various substrates would help clarify the possibility of substances providing nuclei. The studies of Nielsen (1958) on the kinetics of barium sulfate precipitation could, and should, be applied to calcium carbonate.

While a few substances have been studied from the standpoint of the mechanism of the origin, spreading, and interaction of growth layers, this is a blank page for the calcium carbonate polymorphs. The elementary

growth layer has not even been observed nor has the growth rate as a function of supersaturation been measured; either of these would help establish whether growth is by one or both of surface nucleation or screw dislocation mechanisms. When these

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and other fundamental features of the problem are known, we will be able to turn again to evaluating the natural occurrences of aragonite with some hope of understanding them.

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DISCUSSION

PAUL J. SHLICHTA, *Jet Propulsion Laboratory, California Institute of Technology*: Just to add more impetus to the problem, I'd like to suggest some additional complications. First of all the screw dislocation-growth step mechanism is quite the unique mechanism at near equilibrium conditions especially in growth from solution. There are some cases, especially when the crystal is growing from a melt or a high supersatur-

ation where this does not hold, and where growth steps may be spontaneously generated as each preceding step is completed. Now this means that there is a certain class of calcite-aragonite deposition at conditions of relatively high temperature or pressure where this mechanism may be ambiguous. Secondly, and this has been given almost no study, there is the question of getting from the highly hydrated ion in solution to

the solid crystal and how one overcomes the energy of hydration. In some cases this seems to be a surface catalysed dehydration phenomenon and this might also discriminate between calcite and aragonite. Lastly, and this is important because it is usually ignored, whenever growth steps and dislocation mechanisms are obtained, the growth and dissolution of crystals is not a microscopically reversible process at all. This is most especially true in the nucleation phase and more specifically here it means if there is an opportunity for considerable reversal such as with thermal fluctuations during the early stages of nucleation and growth, an enormous amount of discrimination can occur and one species may be entirely eliminated from the process.

CURL: Your comments are all very pertinent. Yes, there are many sources of growth steps: two dimensional nucleation, impurities on the surface, and any irregularities on the surface can be sources of steps for growth. Whatever the source, other factors will interact with the step during growth itself. And, as you indicated, dissolution and growth are not reversible processes. Growth does not usually take place from edge dislocations but dissolution frequently starts from edge dislocations.

With respect to your second question, if we had some idea of the order of reaction of growth of the crystal face, we could say a little more at least about the mechanism of this growth. Some of these crystallizations have been found to be of relatively high order in concentrations of the ions present. This implies that there is some mechanism that involves many of the ion groups getting together before something takes place on the crystal face itself. There is also evidence that in some cases, particularly growth from the vapor, that atoms are capable of landing on the surface at one point and then migrating on the surface to an edge and continuing growth from the edge. There are a tremendous number of possibilities and the details of how the calcium ion and the carbonate ion get down on to the face is certainly not known.

SHLICHTA: In the extreme case, and one almost hates to suggest this, one begins to

worry about the possibility of a monomolecular liquid layer on the surface.

WILLIAM A. BASSETT, *Brookhaven National Laboratory*: I thought I'd tell a story that might be pertinent to this whole growth mechanism problem. It is: Dr. Fankuchen at Brooklyn Polytechnic Institute had an order from *Scientific American* to make an x-ray picture of an ice crystal. He thought this would be fairly easy with the apparatus he had, but when the time came to make the crystal, he used distilled water and unfortunately the crystal he got was very bad. It had many differently oriented zones in it. He tried again with de-ionized distilled water and got an even worse crystal. Finally he used tap water and got a beautiful crystal. The moral is that apparently if foreign ions are present, they will help nucleate a better crystal.

Have you given any thought to the business of growth rates on different faces of calcite? The poisoning of one face rather than another face could cause one form to win out over another form.

CURL: It has occurred to me that the needles of aragonite one finds may have a central screw dislocation. It is also known that many minerals crystallize as needles because of their structure and aragonite may be one of these. However, I have observed needles of aragonite 20 microns in diameter with considerable length. I don't know if an axial dislocation contributes to their growth or not. Different crystal faces will of course act differently with regard to the different impurity ions and organic materials and their effect on generating and spreading growth steps but I haven't given any quantitative consideration to what materials fit on aragonite or calcite surfaces.

WILLIAM E. DAVIES, *U.S. Geological Survey*: I was a little disappointed when you skipped mostly over the biochemistry part. I think that's one of the worst problems we have right now. In the carbonates we have good evidence that the biochemical reactions are extremely important in the precipitation of certain carbonates and I think it is sad that we always treat inorganic minerals as though they could be created only through inorganic processes. One of the biggest problems

in calcite-aragonite deposition may be that of biochemistry. We do know that bacteria are capable of controlling carbonate deposition. At least six forms have been identified. For example, the breakdown of dolomite into huntite, magnesite, and calcite is almost exclusively controlled by certain bacteria. The same process may well apply to aragonite as a catalyst, a poison, or be actually involved in the growth mechanism itself.

CURL: Of course, because of the diversity of living forms, you get a diversity of phenomena with regard to carbonate precipitation. Living organisms are secreting organic agents which may be as effective as any other agent in crystal growth. One of these has been suggested by Stolkowski to be carbonic anhydrase. However, I understand that there are oysters with lots of this that precipitate calcite. The diversity is so great that at present you must file most of it just as interesting phenomena.

DAVIES: I was referring to micro-organisms rather than larger creatures. The thing I'm thinking of is moonmilk. We've been studying moonmilk for quite a while and moonmilk is not a random chemical precipitate at all. It consists of at least four well-recognized minerals produced by six bacteria. There is growing evidence that many of these precipitates, not only in minerals but also in rocks, may be triggered by bacteria. We have obtained huntite, hydromagnesite, and calcite directly from dolomite by these bacteria. A biochemist should investigate to see if aragonite may also be formed.

RICHARD R. ANDERSON, *Bell Telephone Laboratories*: One of the things that causes calcite to fluoresce are the impurity centers. Aragonite fluoresces a different color. Perhaps the type of impurity could be identified by the spectrum of the fluorescence.

GEORGE W. MOORE, *U. S. Geological Survey*: You state that a certain degree of supersaturation with respect to calcite is a necessary but not a sufficient requirement for aragonite formation. As aragonite is 16 per cent more soluble than calcite, perhaps it dissolves faster than calcite. If this is so, pre-

sumably the reverse is also true, and aragonite is precipitated faster than calcite from suitably supersaturated solutions. Shouldn't this factor alone be sufficient to favor aragonite deposition over calcite deposition?

CURL: The fact that aragonite is more soluble than calcite does not mean that aragonite necessarily dissolves more rapidly. The solubility is a matter of equilibrium and the rate is controlled by kinetics. Many factors can affect the latter but ordinarily only temperature, pressure, and composition affect equilibrium. However, Weyl (*J. Geol.* (1958) 66, 163) has shown that the solution of calcite in acid is diffusion controlled. If this is also true for aragonite, which has not been tested, the higher solubility of aragonite would indeed imply a higher rate of solution, per unit surface area, as this would be controlled by the rate of diffusion of ions away from the saturated layer at the surface. Obviously this effect becomes more pronounced as the undersaturation is decreased. At the equilibrium concentration of calcite, aragonite would still be dissolving. Except for cases such as reported by Terjesen, a critical undersaturation for dissolution does not usually exist.

Dr. Schlichta has already pointed out that crystal growth and dissolution are not reversible processes. We cannot deduce that aragonite should precipitate more rapidly even if it should be true that it dissolves more rapidly. In fact, the reverse is more likely, especially at low supersaturations, as the solution must already be supersaturated with respect to calcite before aragonite can even exist. During precipitation calcite always has the advantage of greater supersaturation. If crystal growth were only diffusion limited, calcite would tend to dominate. However, the mechanisms of crystal growth are dominated by activation or nucleation processes. Note that the acicular habit of aragonite means a several fold difference in the rate of growth of adjacent faces even from the same solution. Even if tip growth were diffusion limited, side growth would consequently have to be inhibited by the growth mechanism.

Secondary Mineralization in Wind Cave, South Dakota*

by William B. White and George H. Deike, III

ABSTRACT—Wind Cave contains an assemblage of calcite, hematite, and quartz apparently deposited subaqueously and calcite, aragonite, gypsum, and hydromagnesite deposited subaerially. The boxwork of Wind Cave is a complex consisting of an inner brown calcite fracture-filling, a layer of calcite cemented sediment, an outer lining of clear calcite, and an outer sediment layer. The theory is advanced that the subaqueous minerals were deposited from a warm (100 to 150°C.) solution at high CO₂ pressure. Spectrographic analyses for 9 specimens are given.

INTRODUCTION

Wind Cave is located in Wind Cave National Park, South Dakota in the southeastern Black Hills. Approximately 3 miles of passages have been surveyed and the survey is, as of yet, incomplete. General descriptions of the cave have been written by Tullis and Gries (1938) and Neighbor (1940). The paper by Tullis and Gries contains some excellent mineralogical work. Other work by various authors has appeared as a series of bachelors theses of the South Dakota School of Mines.

Regional Geology — The stratigraphic section near Wind Cave includes the following:

- Precambrian: Igneous rocks.
- Cambrian, Deadwood formation — 60 feet of sandstone and shale.
- Ordovician: Whitewood formation — 80 feet of limestone.
- Mississippian: Englewood formation — 50 feet of limestone.
- Pahasapa formation — 300 feet. Massive gray limestone.
- Pennsylvanian: Minnelusa formation — 115 feet of red sandstone and shale.
- Permian to Jurassic: shale, sandstone, some limestone. 800 to 1000 feet.
- Cretaceous: Dakota group — massive sandstones.
- Plains formation — thick shales. (after Darton and Paige, 1925)

* Contribution number 61-104 of the College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

The sedimentary formations are exposed in bands surrounding the central part of the Black Hills uplift where Precambrian igneous rocks are exposed. The sediments dip gently away from the uplift in all directions. The Paleozoic formations underlie dissected, hilly country next to the igneous rocks. Wind Cave is located in this area. Next outside this dissected country is a topographic low, the Red Valley, developed on shales. This is enclosed by the Dakota hogback. The drainage from the Black Hills escapes through gaps in the hogback onto the Plains.

Wind Cave is developed in the upper part of the Pahasapa limestone, largely in the upper 100 to 150 feet of the formation. This limestone is overlain unconformably by the Minnelusa formation. A Paleozoic karst surface developed on the Pahasapa before the Minnelusa was deposited and old sink holes and cave fills probably dating to Pennsylvanian time are exposed in many parts of the cave.

The Pahasapa limestone is exposed extensively along Wind Cave Canyon upstream from the natural entrance to the cave but most of the cave is under cover of Minnelusa sandstone. At Wind Cave the dip is about 4° SE and the strike about N 40° E. The limestone is moderately well jointed.

The cave area exhibits steep canyon sides and hills with many flat uplands. Whether the flats are erosional or structural is not immediately apparent. Flat surfaces are very

TABLE 1
VERIFIED MINERAL IDENTIFICATIONS

Sample	Description	Results (X-ray)
219.	White floor deposit. Pearly Gates	hydromagnesite
222.	White material from ceiling. Three-Way Stairs.	hydromagnesite
225.	Banded ceiling coating. Garden of Eden.	calcite
241.	White bulbous wall deposits. Lower Attic.	gypsum
243.	"Rotted limestone" wall. Bishop Fowler's Loop.	calcite
252.	White coating on boxwork. Attic.	calcite
254.	White crusts. Attic.	gypsum
257.	Frostwork from sandstone choke. Fairy Palace.	aragonite
258.	White powder growing in thin bulbs. Attic.	hydromagnesite
259.	White powder from floor. Gypsum passage.	gypsum
260.	White wall coatings. Pearly Gates By-pass.	hydromagnesite
265.	Black crystals from boxwork. Attic Sidepassage.	hematite
269.	White filaments under frostwork ledge. Garden of Eden.	hydromagnesite
329.	Frostwork. Rainbow Falls Passage.	aragonite
334.	Black crystals from coarse boxwork. Attic roof.	hematite
360.	Clear water-soluble crystals. Brown Canyon	thenardite
W-15.	Red-brown mass at base of scalenohedral calcite. Near Three-Way Stairs.	hematite

prominent north and northeast and south and southeast of Wind Cave. Oligocene sediments have been mapped on Bison Flat one mile south of Wind Cave. These flats lie at 4170 to 4360 feet above sea level, 250 feet or more above the cave.

Along the streams in the canyons in the Red Valley and on the plains east of the Dakota Hogback two terraces have been identified in many places on the east side of the Black Hills from 50 to as much as 230 feet above the present streams. Along Beaver Creek, to which Wind Cave Canyon is a tributary, terraces at 50 to 60 and 100 to 120 feet above the creek are visible on photographs and topographic maps. Another terrace may lie at 150 feet in the Red Valley, but the visible surface may be structural. The base to which the surface streams near Wind Cave are poised is the elevation of the resistant sandstone of the Dakota Hogback. This is now at 3400 feet at Buffalo Gap, 400 feet below the lowest point in Wind Cave.

Field Work — This study was conducted during the 1959 National Speleological Society Expedition to Wind Cave. Several days were spent examining the mineral deposits in the cave and collecting samples. About

100 specimens were collected and brought to the laboratory for examination and analysis. All samples were catalogued in a permanent collection and will remain on file for future use. All sample numbers in this paper refer to this collection. Lack of an adequate base map made it impossible to map the mineral occurrences so their distribution within the cave remains largely unknown.

Method of Analysis — All samples collected were examined under the binocular microscope. Identification of minerals was by X-ray diffraction. Powder patterns of the unknowns were compared with the patterns of known minerals. The results of these identifications are tabulated in table 1. Changes in the lattice constants of the carbonates were measured by preparing packed slides of finely ground carbonate and scanning them with the diffractometer at 1/8° per minute. This procedure permits measurement of differences of .01° in the Bragg angle.

Spectrographic analyses of a selected suite of specimens were performed using the procedure for major elements developed by Suhr and Joensuu (1962). Briefly the pro-

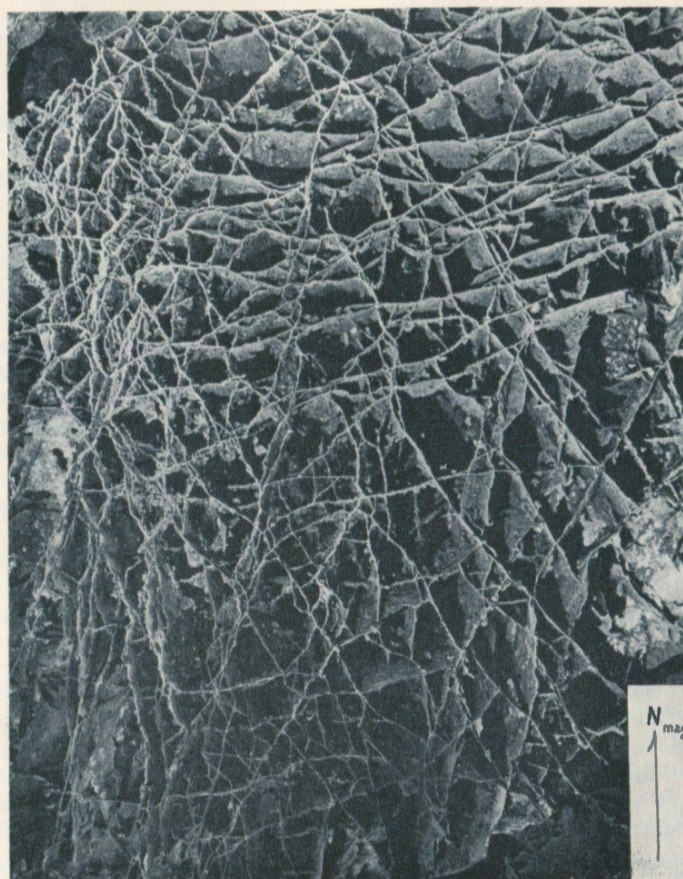


Figure 1

Oriented photograph of typical boxwork in the Blue Grotto Loop.

cedure is: 50 mg. of finely ground sample is mixed with 50 mg. of internal standard (7% Co_2O_3 in LiBO_2) and 250 mg. of $\text{Na}_2\text{B}_4\text{O}_7$. The mixture is fused in a graphite crucible at 1100°C . The resulting borax bead is ground and mixed one to one with powdered graphite. 10 mg. of the final mixture is loaded into electrodes and burned to completion in a Jarrel-Ash 2-meter spectrograph. A segment of the ultraviolet spectrum is recorded on SA-2 plates. The composition of the specimen is determined by comparing the intensity of a selected line of the unknown with a selected line of cobalt.

The accuracy of the analysis was checked by analysing four standard carbonates on the same plates as the samples. A comparison

of our spectrographic results with the reported chemical analyses is given in table 2. S-1 and S-4 were National Bureau of Standards standard carbonates and the chemical analyses given are those of the NBS. S-2 and S-3 are samples of Minnesota lake marls whose composition has been determined very accurately by Goldich, Ingamells, and Thaelmlitz (1959).

Analytical results for nine selected Wind Cave specimens are given in table 3. Calcium and aluminum were determined by plotting analytical curves based on the standards. Thus there is no cross check on their accuracy and the results quoted may not be as good as those quoted for the other elements.

TABLE 2
COMPARISON OF SPECTROSCOPIC ANALYSES OF STANDARDS
WITH CHEMICAL ANALYSES

Standard	MnO		MgO		Fe_2O_3	
	Spec.	Chem.	Spec.	Chem.	Spec.	Chem.
S-1: N.B.S. Argillaceous limestone	.039	.038	2.1	2.19	1.5	1.63
S-2: HR 5-7 Lake marl	.125	.13	1.2	1.23	.26	.24
S-3: CNC 1-S Lake marl	.097	.10	1.2	1.11	.83	.82
S-4: N.B.S. No. 88 Dolomite	.006	.006	--	21.48	.20	.084

TABLE 3
SPECTROGRAPHIC ANALYSES OF WIND CAVE MINERALS

Sample (2)	W-7	224	226	249	265	323C	323R	329	342
MnO	.015	.0025	.025	.005	.077	.0039	.025	.0085	.0074
Fe_2O_3	.29	.23	.14	.054	.18	.25	.14	.068	.17
MgO	.23	.38	.34	.25	.11	1.00	.52	.29	.42
CaO	53.	50.	51.	56.	51.	54.	54.	49.	54.
Al_2O_3	.18	.13	.72	.063	.11	.066	.21	.20	.10

NOTES ON TABLE 3

(1) All results are given in weight percent.

(2) Descriptions of the samples are:

- W-7: Scalenohedral calcite complex with brown zoned scalenohedrons.
 224: Clear stalactite from Fairy Palace Loop.
 226: Boxwork from Pearly Gates By-pass. Mostly pink core material.
 249: Massive clear scalenohedral crystals with no "seeds".
 Near Historic Entrance
 265: Coarse brown calcite (enlarged boxwork core?) with coarse intergranular hematite from Attic Side Passage.
 323C: Transparent outer boxwork coating.
 323R: Pink boxwork core.
 329: Frostwork crystals (aragonite) from Rainbow Falls Area.
 342: Small clear calcite crystals containing black "seeds" from cluster of crystals in Attic Ceiling.

Acknowledgments — We are grateful to the Superintendent and staff of Wind Cave National Park for their cooperation in allowing this work to be carried out. Members of the NSS Wind Cave Expedition were very helpful in conducting the field work. Mr. Norman Suhr advised on setting up the spectrographic analyses. J. A. Stellmack provided the close-up photographs used in this report. Financial support for the laboratory work was provided by the Mineral Industries Experiment Station of the Pennsylvania State University.

SUBAQUEOUS DEPOSITS

Boxwork and Related Crystal Coatings — Wind Cave was set aside as a National Park because of the fine display of boxwork that covers many walls, floors, and ceilings. These deposits were first well described by Tullis and Gries (1938). Bretz (1942) listed boxwork as a solutional feature of phreatic origin — arguing that the fragile fins of the boxwork cores could not have withstood the turbulent flow of free-surface streams. While very common in Wind Cave, boxwork is also reported to occur in lesser quantities in the

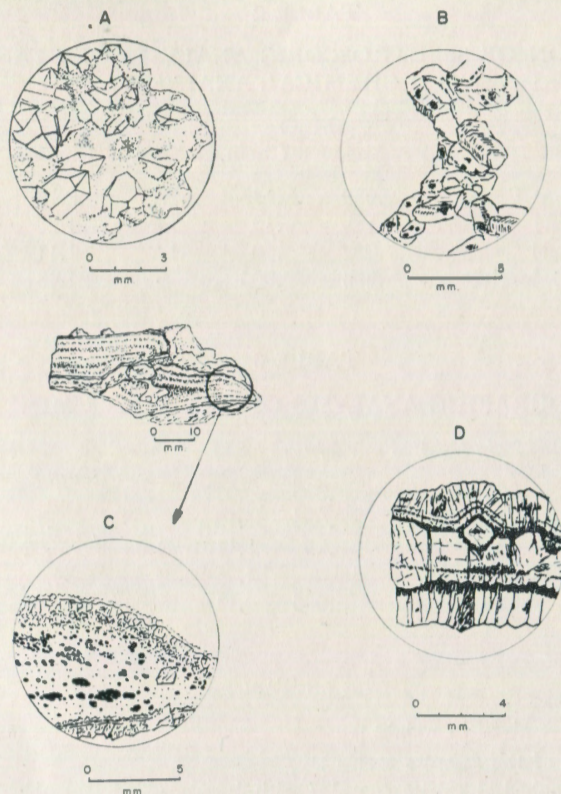


Figure 2

Microscope sketches of minerals:

- A. Euhedral quartz embedded in pink calcite sediment.
- B. Clear calcite crystals with black hematite "seeds".
- C. Complexly bedded sediment—mostly fine-grained calcite with black specks.
- D. Thin section showing outer crystal lining, boxwork core, and faint trace of "inner core".

other caves of the Black Hills (Tullis and Gries, 1938). It is uncommon in the limestone caves of other areas.

The A.G.I. Glossary defines boxwork as follows: "Limonite and other minerals which originally formed as blades or plates along cleavage or fracture planes and then the intervening material dissolved leaving the intersecting blades or plates as a network". The boxwork of Wind Cave follows this definition (fig. 1). Boxwork differs from other protruding bedrock remnants such as clay fins and simple mineral veins primarily by its network pattern.

Although the Wind Cave boxwork is of calcite, there seems no good reason for limiting the definition to this mineral or to limonite. Skrivanek and Valasek (1959), for example, have published photographs of a boxwork of silica occurring in the Bozkov Cave in Czechoslovakia.

Where boxwork can be traced into solid bedrock, the bedrock fracture filling is usually paper-thin. It enlarges when it emerges from the rock with no noticeable change in color or texture. Cross-sections of boxwork usually show a core thickness of 1 - 2 mm. —much thicker than most bed-

rock veins. Certain of the pink cores show a very thin "inner core" demarked by slight changes in texture. Individual calcite crystals in the pink cores are up to 2 - 3 mm. in size. Cleavage planes are continuous through the entire core. The thickening of the core without any break in crystal continuity suggests that some deposition of calcite onto pre-existing nuclei took place contemporaneously with the solution of the limestone walls. A thin layer of pink-brown core material is commonly observed extending from the core separating the cave wall from the remainder of the deposit. A thin section (fig. 2-d) shows the faint "inner core" by change of texture although crystal continuity is complete across the entire core.

The boxwork core is often coated on upward facing surfaces with a fine-grained pink sediment — the red crystalline limestone of Tullis and Gries.

Above the inner sediment coating and directly against the core on the lower side is the outer crystalline lining. The outer lining consists of clear calcite crystals averaging 1 - 3 mm. in size. The outer crystal coating has definitely been deposited since the development of the cave. At the crystal-limestone interface where the inner core extends into the wall rock as a vein filling, the outer lining extends over the wall. On the lower sides of the boxwork blades there is a definite break in crystal continuity between the core and the outer lining.

A second and much thicker layer of sediment occurs on most upward facing surfaces in the cave. The outer sediment is developed to thicknesses of several centimeters and is often delicately stratified. The deposition of the outer sediment seems to have been the last event to occur while the cave was still water-filled. Figure 3 is a photograph of a cross-section of a boxwork fin in which it can be seen that the upper crystal lining is delicately layered while the lower crystal lining consists of coarse crystals. Perhaps some of the second sediment layers were deposited at the same time as the outer crystal linings.

Figure 4 is a schematic drawing of a boxwork cross-section showing the main features of the deposit.



Figure 3

Photograph of typical boxwork cross-section. Wire is one centimeter long.

Geodes and Scalenohedral Crystal—

Geodes, often 5 to 10 cm. in diameter, occur in a room near the natural entrance and scattered throughout the cave. A typical geode is pictured in figure 5. A central dark ring possibly marks the old boundary of the pocket in the bedrock. Inside is a layer of coarse clear scalenohedral calcite with individual crystals from 1 to 5 cm. long. Many of the geodes are partly or completely sediment filled, often as in the case of figure 5, with rounding of edges and tops of the scalenohedrons by resolution. The outsides are coated with a layer of calcite crystals in the same manner as the boxwork and this in turn is overlain on its upper surface by the outer sediment.

Some roughly spherical objects are found that are not geodes but are merely lumps of sediment stuck at interstices in the boxwork and covered with the outer crystal coating.

Coarse crystal linings of scalenohedral calcite (dogtooth spar) are occasionally found particularly in the upper levels of the cave.

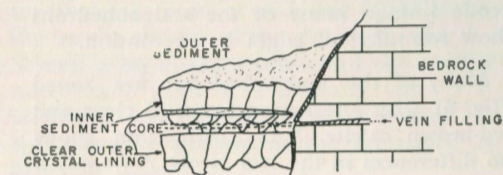


Figure 4

Sketch showing typical parts of the boxwork deposition sequence.

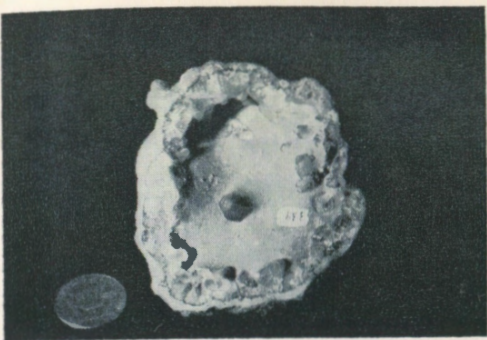


Figure 5

Geode from "Alvin's Workshop" near natural entrance.



Figure 6

Zoned scalenohedral calcite crystals.

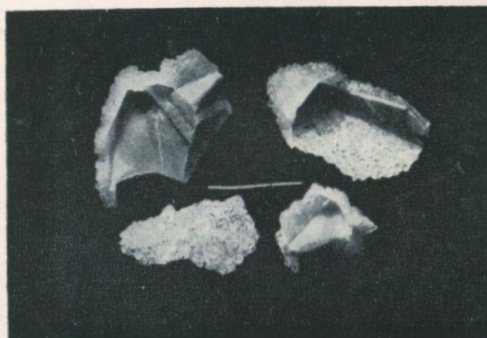


Figure 7

Casts removed from scalenohedrons showing inner sediment layer and outer crystal lining. The outer crystal lining is partly euhedral quartz.



Figure 8

Well-developed fine-grained calcite sediment showing impressions of calcite scalenohedrons.

Nowhere do the crystal linings become so profuse as those in Sitting Bull Crystal Cave, for example. Individual scalenohedrons are found up to 2 cm. in length. They characteristically grow with the c-axis (the long axis of the scalenohedron) perpendicular to the growth surface. As in the case of the geode linings, many of the scalenohedrons show rounding of edges by re-solution.

Many of the scalenohedrons are zoned (fig. 6) with alternating layers of clear and red-brown calcite. X-ray diffraction shows no differences in the two layers. An analysis of a scalenohedron is given in table 3.

Figure 7 is a photograph of casts that were pulled from some scalenohedrons. They

clearly show that the scalenohedrons grew concurrently with the boxwork cores*. A thin (1 - 3 mm.) layer of pink sediment has been deposited directly over the calcite crystal. On the outside is a 1 - 2 mm. layer of clear calcite crystals exactly similar to the outer crystal lining of the boxwork. Masses of white to pink black-speckled limestone were found containing the impressions of scalenohedrons (fig. 8) suggesting that in places the first sediment layer reached considerable thicknesses.

* Dwight Deal has called our attention to the fact that the scalenohedrons in Jewel Cave and Sitting Bull Crystal Cave are associated with the clear outer crystal linings whereas in Wind Cave they are associated with the boxwork cores.

The corners of the scalenohedral impressions in the crystal casts and the limestone molds are sharp indicating that the solutional rounding of the exposed scalenohedrons took place after the first sediment layer was deposited.

Irregular Crystallization — The higher passages of the cave, particularly the Attic and its side branches and the high level passages above the Pearly Gates have ceilings impregnated with complex masses of crystals. Irregular clumps of scalenohedral calcite, masses of sediment, and poorly developed boxwork are common.

A typical assemblage includes a matrix of pink calcite of 1 - 3 mm. grain size — similar to the boxwork core — interspersed with 1 - 3 mm. grains of hematite. The x-ray diffraction pattern of hematite shows considerable line broadening indicating a true crystallite size of about 10^{-6} cm. Thus while the grains are coarse and exhibit flat faces, they are not large hematite crystals.

Hematite also occurs as small grains in the boxwork cores. It is not limited to the "inner core" but characteristically forms near the edge of the core; never in the outer crystal lining. Some masses of pink to clear calcite crystals from the Attic have .01 to 0.1 mm. black hematite "seeds" in the centers of the 1 - 5 mm. calcite grains. An analysis of these crystals (fig. 2-b) is given in table 3. The total iron content of the crystal is .17%; probably just enough to account for the seeds.

Quartz occurs in several of the complex assemblages as euhedral transparent crystals 1 - 3 mm. in size (fig. 2-a). It occurs in an irregular mass of calcite crystals, sediment, and hematite and is apparently authigenic, having formed from the same solutions as the hematite and carbonates.

SUB-AERIAL DEPOSITS

Dripstone — Small stalactites, stalagmites, and a little flowstone occur in an area on the Fairy Place Loop, at the end of the Rainbow Falls Trail, and at the Bleeding Heart in the Garden of Eden. An analysis of a typical small stalactite from the Fairy Palace Area is given in table 3, showing the stalactite to be a very pure calcite with less than one percent total impurities.



Figure 9

Aragonite clusters growing on tips of globulites.

The few sparse deposits of dripstone all occur in parts of the cave lying under Wind Cave Gulch or its tributaries. The lack of dripstone in other parts of the cave is likely due to the overlying Minnelusa sandstone sealing off the limestone from ground water circulation and also to the general arid climate of the region.

Globulites and anthodites — Botroidal masses, known locally as "popcorn", and radiating clusters of aragonite crystals, known as "frostwork", occur irregularly in clusters in many parts of the cave. The "popcorn" (a speleothem usually referred to as the globulite) appears to have a structure similar to globulites from other limestone regions. The nodules range in size from 1 to 10 mm. supported by stalks about 1 mm. in diameter. In cross-section they show a layered structure with no evidence for a central canal.

The aragonite crystals commonly occur as "frostwork ledges" — areas a meter or more wide. The crystals grow uniformly over the surface. The crystals are white and grow in acicular groups several centimeters long. The anthodites and globulites are usually found together; aragonite crystals are found growing on the nodules of the globulites (fig. 9). Several x-ray analyses confirmed the careful microscopic work of Tullis and Gries and identified the frostwork as aragonite. A spectroscopic analysis of the frostwork is given in table 3.

Gypsum — Gypsum is common in much of the northern part of the cave, particularly in the passages underlying the Attic, and in

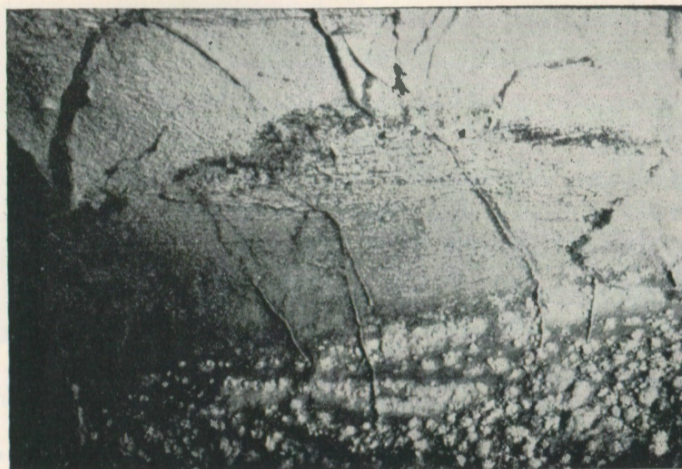


Figure 10
Small piles of hydromagnesite "moonmilk" in Pearly Gates Bypass.

the Pearly Gates area. Identification was confirmed by x-ray diffraction. Four forms are present: (1) Small clumps of irregular crystals less than 1 mm. across. (2) "Cave cotton" consisting of 10 to 20 cm. diameter tufts of thin hair-like crystals of selenite. (3) Straight selenite needles, multiple twinned, about 1 mm. in diameter and several centimeters long. (4) Gypsum crusts of curved gypsum crystals a few millimeters to a few centimeters long. The cotton and selenite needles are rare but crusts occur commonly as thin coatings on floors and walls. *Moonmilk* — Small piles of fine-grained white powder, particularly common in the Pearly Gates Bypass (fig. 10), were identified by x-ray diffraction as hydromagnesite ($3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$) one of the so-called moonmilk minerals. The x-ray pattern is identical with the data published by Murdoch (1954). The Wind Cave hydromagnesite is very fine grained and no crystals are visible under the microscope. However the x-ray peaks are sharp indicating that the material is well-crystallized with a probable grain size of 10^{-5} to 10^{-4} cm.

A particularly significant specimen was discovered on the floor below the frostwork ledge beside the tourist route in the Garden of Eden. The hydromagnesite occurs as a thin curled ribbon of white powder and was apparently the ash from a burnt strip of

magnesium ribbon such as might have been used to illuminate the frostwork display above. The occurrence is very suggestive that the highly activated MgO formed from burning magnesium reacted directly with the cave atmosphere to form hydromagnesite and offers an insight into the thermodynamic stability of moonmilk.

Moonmilk has been extensively investigated by Pobeguín and her co-workers in France (Geze, 1961). They have suggested that moonmilk is primarily a product of the action of microorganisms although the chemical stability of moonmilk in general is still unknown.

Garrels, Thompson, and Siever (1960) have recently published thermochemical data on many carbonate minerals. They have constructed a phase diagram showing the stability range of calcite, dolomite, magnesite, and hydromagnesite as a function of the $\text{Ca}^{++}/\text{Mg}^{++}$ ratio and the carbon dioxide pressure for phases crystallizing from water solutions. The diagram indicates that hydromagnesite is not a stable phase in equilibrium with atmospheric CO_2 and water for any magnesium ion concentration.

However, Wind Cave is remarkable dry. No liquid water is present in any of the moonmilk areas. Therefore if hydromagnesite is forming in the cave today under

equilibrium conditions, it must be in equilibrium with a vapor phase — the CO_2 and H_2O in the cave atmosphere — only. The stability relations in this case are completely different from those in the case of solutions. We have calculated a phase diagram for the solid-vapor equilibrium at 25°C . from the thermochemical data (fig. 11). The details of the calculation are given in an appendix.

If one determines the CO_2 and H_2O pressures in the cave atmosphere, the stable solid phase is immediately given by the diagram. In an open cave the CO_2 pressure would vary very little from the atmospheric pressure of $10^{-3.5}$ bars. This limits the conditions to the crossed line on the diagram. If the relative humidity reaches 100%, liquid water would condense, and the hydromagnesite would dissolve and be re-precipitated as magnesite. Only at the low water vapor pressure of $10^{-3.5}$ bars would hydromagnesite dehydrate to magnesite in the solid state.

Thus we believe that the occurrence of hydromagnesite in Wind Cave can be explained by the seepage of magnesium-rich solutions into the dry cave with resultant evaporation of water and deposition of moonmilk without recourse to any additional biochemical mechanism.

Water-soluble Sulfates — In Brown Canyon occur very sparse water-clear curved crystals up to 1 cm. long and tufts of clear hair-like needles several cm long. They grow from bedrock surfaces and breakdown blocks and are water soluble with a distinct salty taste. They melt easily in the flame of a carbide lamp. Although x-ray analysis shows the sample in the laboratory to be thenardite, $\text{Na}_2\text{SO}_4 \cdot \text{V}$, it is clear that the mineral occurring in the cave is a sodium sulfate hydrate such as mirabolite, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, described by Benington (1959) in the Flint Ridge Cave System. Mirabolite decomposes very easily to thenardite and certainly would not have withstood transportation un-refrigerated in the August heat.

CHEMISTRY OF DEPOSITION

Wind Cave (and other caves of the Black Hills) are uniquely different from other limestone caves of the writers experience. To summarize, the differences are:

1. The extensive occurrence of coarse cal-

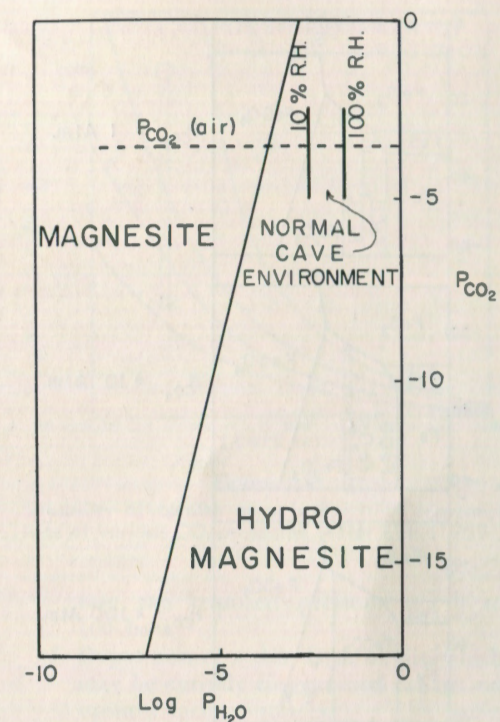


Figure 11
Log PCO_2 - log PH_2O diagram for the dehydration of hydromagnesite.

2. cite vein fillings (the boxwork cores).
 2. Extensive deposition of euhedral calcite apparently under sub-aqueous conditions (outer crystal linings) with underlying and overlying fine-grained calcite rich sediment.
 3. The occurrence of hematite and euhedral quartz apparently in equilibrium with the solutions depositing the calcite.
- A chemical mechanism must be devised that will account for the mineral assemblage.

Temperature of Deposition — Many of the analyses were performed in hopes of finding some information on the temperature of deposition. The carbonate minerals proved devoid of useful information. Goldsmith, Graf, and Joensuu (1955) suggest that high magnesium content (greater than 5%) of a calcite implies a higher temperature of deposition. The magnesium concentration in solid solution (in absence of

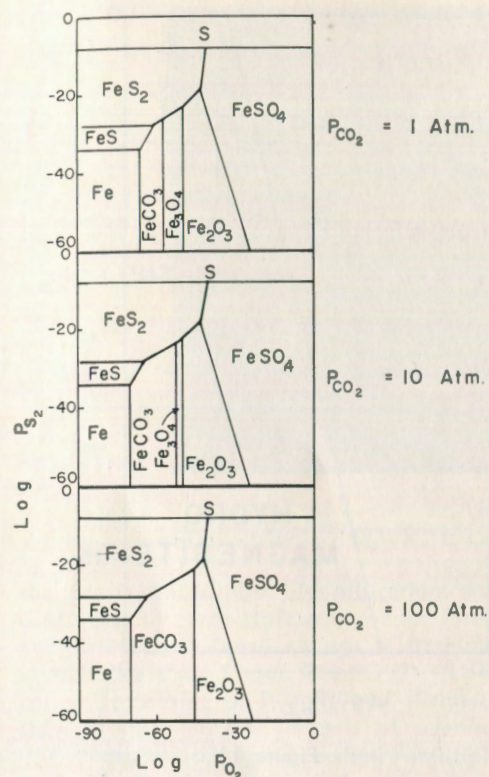


Figure 12

P_{O_2} - P_{S_2} isothermal sections at 127° C. at various carbon dioxide pressures for the system Fe-C-S-O. Derived from Holland (1959).

significant amounts of iron and manganese) can be determined by the shift in d-spacing of the calcite x-ray peaks. Measurements on the 014 and 212 peaks of a suite of Wind Cave calcites suggested magnesium contents of 4 to 5% in the boxwork cores. These results were not born out by the spectrographic analyses. From table 3 it can be seen that the maximum magnesium concentration is about 1%—much too low to indicate a high temperature of origin. The reason for the inconsistency between the measured spacings and the magnesium concentration is not known.

The presence of euhedral quartz is an indicator of a high temperature solution. SiO_2 precipitated from cold water usually comes out as amorphous silica and indeed large amounts of opal were reported by Tullis

and Gries to be associated with the later frostwork deposits. Solution temperatures in the range of 100° to 200°C. are necessary for the growth of quartz crystals.

Hematite is common in the boxwork cores and in the irregular crystallizations. This is unusual — the common iron mineral in caves is goethite ($FeOOH$). Schmalz (1959) has shown that the goethite-hematite phase boundary at atmospheric pressure is 130°C. with the dehydration temperature increasing with increasing water pressure to 175°C. at 1000 bars. Thus the presence of hematite rather than goethite suggests a temperature of crystallization greater than 130°C. It should be pointed out that hematite is metastable in the present cave environment. Cold ground water could react with it to form the stable goethite.

Pressure of Deposition — The phase assemblage calcite-hematite can provide additional information about the environment of deposition. One must first inquire how the iron was transported into the deposit. Hematite is extremely insoluble. In a predominately carbonate assemblage, the iron likely came in as $FeCO_3$ in solution and precipitated first as siderite which then oxidized to hematite.

Three isothermal sections at 127°C. for the system Fe-C-O-S taken from Holland (1959) are given in figure 12. The diagrams were derived for solid-vapor reactions only and ideally should also include water as a component and pH as a variable since deposition is from water solution. However, since pH is buffered close to the neutral point by the limestone and there are no hydrated phases present, the diagram as given is accurate enough for the purpose.

The diagram shows which minerals are stable at a particular selection of partial pressure of CO_2 , O_2 , and S_2 at constant temperature and total pressure. A stability field for siderite does not appear at 127°C. until P_{CO_2} reaches 10 bars. The oxygen pressure must be in the order of 10^{-60} bars. The siderite field adjoins the field of hematite and thus a slight rise in P_{O_2} will cause the oxidation of $FeCO_3$ to Fe_2O_3 . Siderite is stable at lower CO_2 pressures at lower temperatures but this is inconsistent with other criteria. At higher temperatures $FeCO_3$

is only stable at extremely high CO_2 pressures.

The absence of any sulfide phases from the Wind Cave assemblage further suggests that the sulfur pressure was less than 10–20 bars. It is very unlikely on this basis that the solutions originated as residual fluids from ore-forming hydrothermal solutions since PS_2 would have been much higher. High PS_2 and high PO_2 would have oxidized the iron to $FeSO_4$ which is soluble and the iron containing phases would not have appeared at all.

The implied high CO_2 pressures are consistent with a mechanism of carbonate deposition. Consider the solubility of calcite at higher temperatures (figure 13 taken from Ellis, 1959). If a saturated carbonate solution is allowed to cool at constant pressure, calcite becomes more soluble, not less. Furthermore it is necessary to have a high CO_2 pressure to dissolve a significant amount of calcite at these temperatures.

The most reasonable way to explain the deposition of the Wind Cave carbonates is to assume that crystallization took place by loss of CO_2 from the pressure drop occurring when the solutions moved into the cave. By allowing the pressure to fall from an initial value of about 50 bars to atmospheric pressure, 80% of the dissolved $CaCO_3$ would precipitate.

In summary: The evidence indicates that Wind Cave minerals were deposited from solutions at 150° to 200°C. with $P_{CO_2} = 10$ to 100 bars, and P_{O_2} less than 10^{-50} bars. Crystallization of calcite and siderite took place isothermally with loss of CO_2 . Siderite was then oxidized to hematite by the higher oxygen pressures present in later cave filling solutions.

Sequence of Deposition — The apparent sequence of the events in the cave is:

1. Formation of boxwork cores and a few geodes by fracture filling within the limestone.
2. Solution of the limestone to form the cave leaving the less soluble boxwork standing out in relief, with contemporaneous deposition of the thick part of the boxwork core. A depth of burial of 300 to 3000 feet is necessary to main-

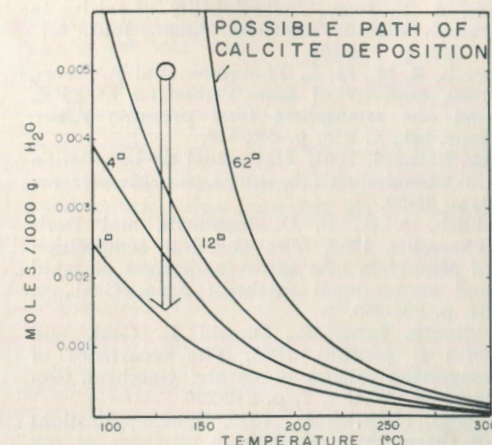


Figure 13

Solubility of calcite as a function of temperature at various CO_2 pressures. After Ellis (1959).

tain the required pressure of 10 to 100 bars.

3. Deposition of a thin layer of silt, which may be entirely fine-grained calcite, on upward facing surfaces.
4. Deposition of a complex layer of coarse calcite on most surfaces.
5. A second and more intensive period of deposition and cementation of silt.
6. Draining of the cave and deposition of sub-aerial speleothems.

We have deliberately refrained from speculating on the correlation of the sequence of cavern development with the sequence of mineralization. The conclusions of this paper are highly tentative and await collaborative evidence from a detailed field study of the deposits. Only when the deposits in the cave have been mapped in detail will it be possible to deduce the complex history of cavern development.

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APPENDIX

CALCULATION OF THE STABILITY FIELD OF HYDROMAGNESITE

The free energies of formation are:

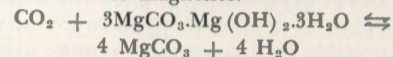
Magnesite — 242.2 kcal./mole (Kubaschewski and Evans)

Hydromagnesite — 1108.3 (Garrels, Thomson, and Siever)

Water Vapor — 54.64 (Latimer)

Carbon Dioxide — 94.24 (Latimer)

We make the assumption that hydromagnesite is in equilibrium with a moist, CO_2 - bearing atmosphere at one bar total pressure and 25°C. but that liquid water is not present. The expected reaction is one in which hydromagnesite reacts with CO_2 from the atmosphere and loses water to become magnesite:



In this simplified calculation the possibility of formation of nesquehonite or artinite is not

considered. The equilibrium constant for the reaction is written:

$$K = \frac{a^4(\text{mag}) \cdot P^4(\text{H}_2\text{O})}{a(\text{hyd}) \cdot P(\text{CO}_2)}$$

If the solid phases are stoichiometric, their activity will be unity. The change in free energy of the reaction is given by:

$$\Delta F = -RT \ln K$$

The free energy of reaction must balance the change in free energy of formation:

$$-RT \ln P^4(\text{H}_2\text{O}) / P(\text{CO}_2) = 4\Delta F^\circ(\text{mag}) + 4\Delta F^\circ(\text{H}_2\text{O}) - \Delta F^\circ(\text{Mag}) - \Delta F^\circ(\text{CO}_2)$$

Inserting numerical values and reducing:

$$4 \log P(\text{H}_2\text{O}) = \log P(\text{CO}_2) - 11$$

This is the equation of a straight line if plotted on a log-log scale and becomes the phase boundary of figure 11. Only on the line can the two solid phases exist in equilibrium with a vapor.

DISCUSSION

RICHARD R. ANDERSON, *Bell Telephone Laboratories*: You apparently haven't looked very far for boxwork. I have observed boxwork in Dreibilbis Cave in Southeastern Pennsylvania.

DEIKE: It all depends on what you define as boxwork. Clay fins, quartz veins, and calcite

veins all stand out in relief on cave walls. If these have intricate patterns they might be called boxwork. I would suspect that the Dreibilbis material is of this nature. As far as I know, boxwork of the type common in the Black Hills has never been reported elsewhere.

RANE L. CURL, *Shell Development Co.*: Why did the limestone dissolve and the boxwork not?

DEIKE: There could be several reasons. Firstly, large crystals dissolve at a slower rate than limestone and thus the limestone wall would retreat faster. Secondly, the boxwork

material has a lower solubility than the calcite of the wall rock.

ANDERSON: How do the veins differ from calcite?

DEIKE: They are calcite but contain a few percent essential magnesium carbonate in solid solution thus lowering their solubility.

Hexagonal Stalactite from Rushmore Cave, South Dakota

by William A. Bassett and Allen M. Bassett

ABSTRACT—A stalactite having the form of a hexagonal prism was found in Rushmore Cave near Rapid City, South Dakota. The broken end is a cleavage plane inclined to the axis of the stalactite indicating that the stalactite is a single crystal of calcite. The dimensions of the stalactite and the pattern revealed in the cleavage face suggest that it formed as a monocrystalline soda straw which served as a seed crystal for subsequent calcite deposition on the exterior. Two soda straw stalactites from the Ohio Caverns, West Liberty, Ohio were found to be monocrystalline with their c-axes vertical. A soda straw grows at its tip by deposition of CaCO_3 from the drop hanging there. It is suggested that in soda straws calcite's rapid growth in the c direction favors domains with vertical c-axes because they grow rapidly into the drop and eliminate domains having different orientations.

LOCATION AND DESCRIPTION

A stalactite in the shape of a hexagonal prism was discovered in the Rushmore Cave located on the east flank of the Black Hills uplift south of Rapid City, South Dakota. It occurs in a part of the cave called "the Vegetable Garden" among many of the usual tapered stalactites with generally circular cross-sections and radial crystallinity. Its lower end had been broken off along a cleavage surface (fig. 1). The hexagonal stalactite was inaccessible for measurement of dimensions and interfacial angles. The specimen could not be collected nor could the broken off part be found. The prism is estimated to be four or five inches long and half an inch across. The cleavage face is a single plane oblique to the long axis of the stalactite indicating that the stalactite is a single crystal of calcite. The pattern revealed in the cleavage surface is an irregular circle with a diameter about half that of the prism. The circle encloses somewhat darker calcite with a spot of very dark material slightly off center.

Other examples of stalactites showing external crystal form have been described by Snyder (1951) and Halliday (1959). The genesis of these stalactites poses an interesting problem. Any explanation must account for their relative rarity.

INTERPRETATION OF THE OBSERVED FEATURES

The most diagnostic features are to be found in the pattern shown in the cleavage face at the broken end of the stalactite. The circle is about the right diameter to be the cross-section of a relict soda straw stalactite. The difference in color between the calcite inside the circle and the calcite outside the circle also suggests that the calcite on the outside formed at a different time and under different conditions. The slightly eccentric dark spot in the circle appears to have been the internal tube which carried the solution at the time the soda straw formed. Although it was difficult to determine, the tube seems to be completely filled. The calcite outside the circle appears to be an overgrowth on a soda straw. It may have started depositing when the central tube became clogged and solution began to run down over the exterior of the soda straw.

The uniform diameter of the stalactite, which is slightly more than the diameter of a typical soda straw, strongly supports the origin by overgrowth on a soda straw. This explanation is similar to those offered by both Snyder (1951) and Halliday (1959).

OBSERVATIONS ON SODA STRAWS FROM OHIO

Two soda straw stalactites loaned to us by Mr. I. E. Smith of the Ohio Caverns, West



Figure 1
Hexagonal stalactite, Rushmore Cave, South Dakota.

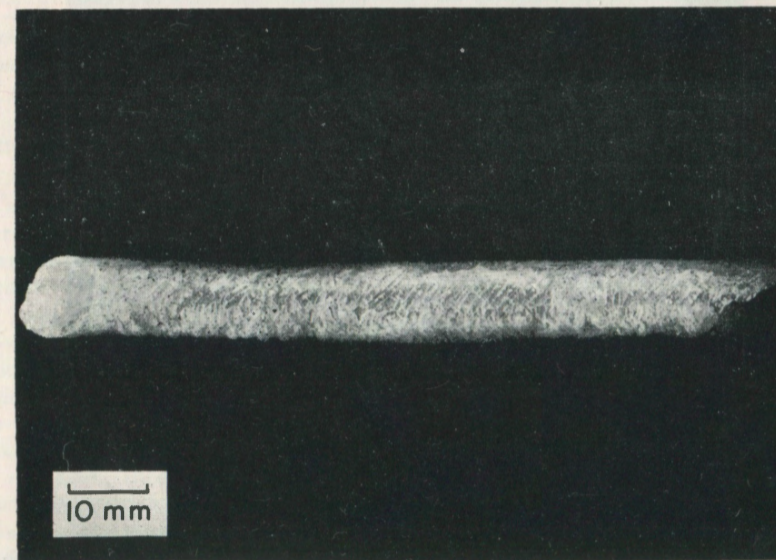


Figure 2
Soda straw stalactite, Ohio Caverns, Ohio.

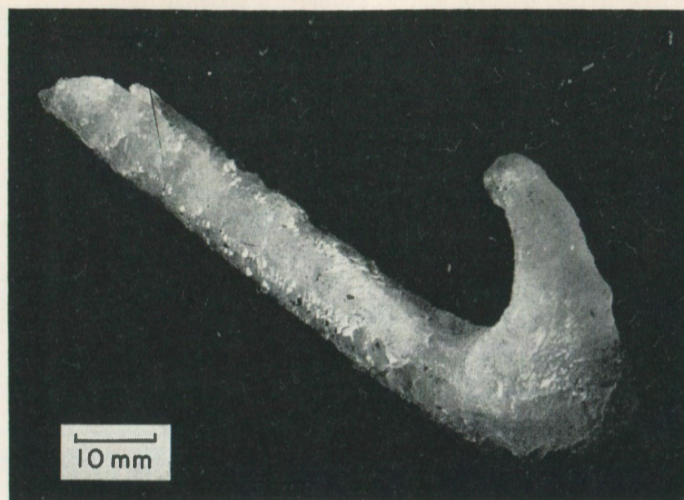


Figure 3
Helictite,, Ohio Caverns, Ohio

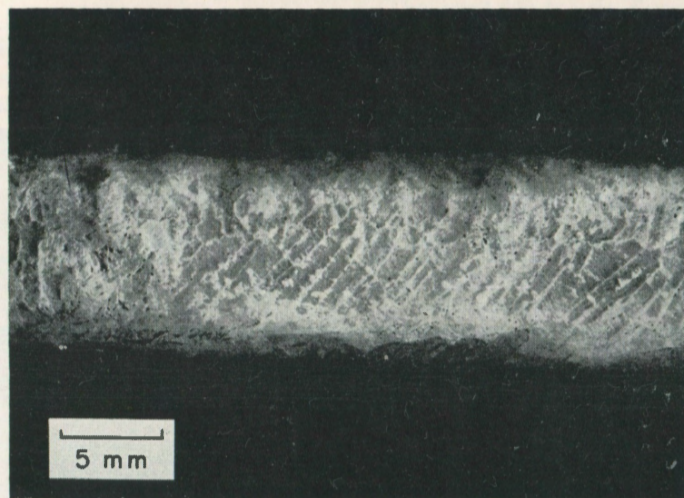


Figure 4
Cleavage pattern in the wall of the soda straw stalactite from Ohio Caverns, Ohio.

Liberty, Ohio have provided some very useful information about the formation of monocrystalline stalactites (figs. 2 & 3). One of these is a straight cylindrical stalactite with an eccentric hollow tube. A chevron pattern can be seen on the thin wall of the tube (fig. 4). This pattern is due to rhombo-

hedral cleavage and conforms to the cleavage surface at the broken end. There are no crystal faces developed on the sides of this stalactite.

The other stalactite is a helictite formed by the growth of a nonvertical projection at the end of a soda straw. Above this pro-

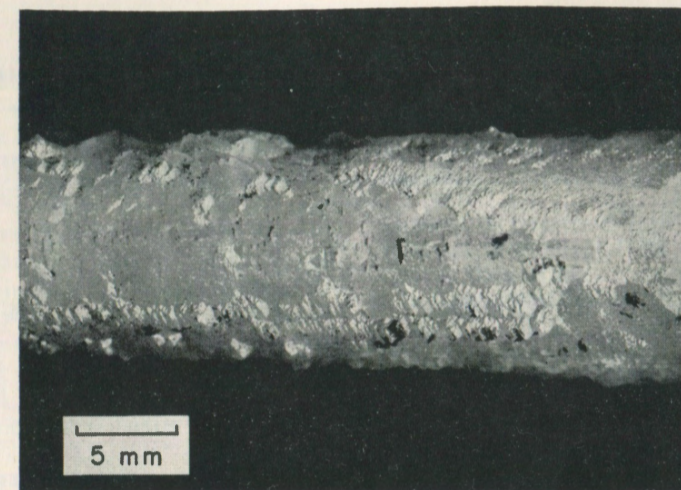


Figure 5
En echelon rhombohedral faces on the surface of the helictite from Ohio Caverns, Ohio.

jection, where the stalactite is a simple soda straw, a number of poorly formed faces can be observed on the surface of the stalactite (fig. 5). Both first order and second order prism faces as well as some en echelon rhombohedral faces were determined by means of a two circle goniometer.

MECHANISMS PRODUCING HOLOCRYSTALLINE STALACTITES

Figure 6 is a diagrammatic representation of the early stages of soda straw formation. In the earliest stage, calcite is deposited in a ring around the source conduit and continues to form by extension of the randomly oriented crystal grains of the limestone upon which growth begins. The direction of most rapid growth in calcite is along the c-axis. As a drop of supersaturated solution deposits calcite on a surface of randomly oriented domains, those domains having their c-axes nearly vertical, and therefore extending in the direction of the solution, grow more rapidly than the others. The domains having less favorable orientations will grow more slowly and will be eliminated (fig. 7).

Eventually, under ideal circumstances, only one calcite domain is left and the entire stalactite becomes a single crystal with

vertical c-axis. The faintly hexagonal cross-section and the irregular but somewhat flat faces sometimes evident in soda straws cannot, it appears, develop good hexagonal prisms because soda straws are developed by deposition in a ring from the drop at the bottom end of the stalactite.

DEVELOPMENT OF GOOD EXTERNAL FORMS

External form in the case of the Rushmore Cave stalactite seems to have developed when the internal conduit became clogged and the solution flowed over the outside of the soda straw depositing calcite which acquired the orientation of the calcite in the soda straw (fig. 8). Certain conditions may have aided in the extension of the single crystal orientation. Such conditions may have been 1) a solution free from foreign ions such as might cause nucleation of differently oriented domains, 2) high water vapor pressure in the cave keeping the evaporation of water at a minimum, 3) uniform flow of solution over the entire external surface of the stalactite, and 4) low carbon dioxide vapor pressure permitting rapid loss of carbon dioxide from the solution thus allowing it to become supersaturated over the whole surface of the stalactite.

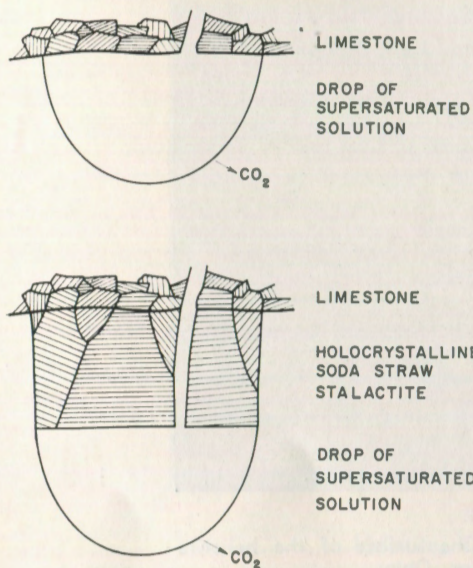


Figure 6

Diagrams illustrating the probable mechanisms resulting in a soda straw consisting of a single crystal of calcite with its c-axis vertical.

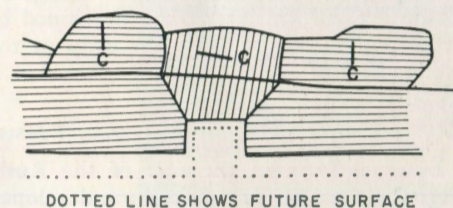


Figure 7

Diagram showing in detail the process of elimination of calcite domains with nonvertical orientations.

CONCLUSION

The following sequence of events is believed to have led to the formation of the hexagonal stalactite found in Rushmore Cave:

1. The formation of a monocrystalline soda straw,
2. A change from internal flow to external flow of solution,

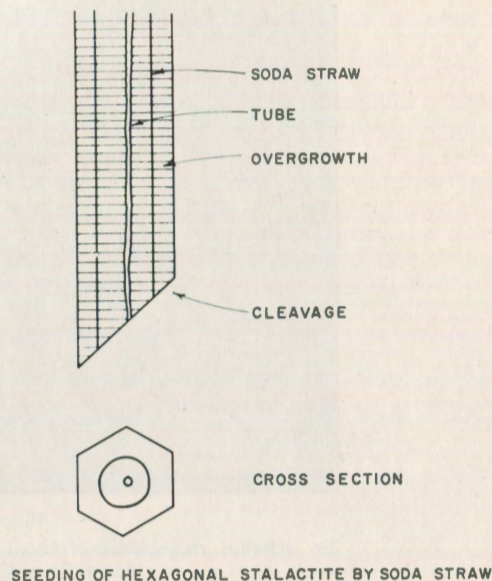


Figure 8

Diagram indicating the probable internal structure of the hexagonal stalactite in Rushmore Cave.

3. Sufficient purity and uniformity of solution to extend the original orientation into the newly deposited calcite.

No one of the circumstances is rare by itself. It is the combination of these circumstances that accounts for the rare occurrence of hexagonal stalactites.

ACKNOWLEDGMENTS

The authors wish especially to thank the owners of the Rushmore Cave for permitting photographs of their speleothems to be taken and to the owners of the Ohio Caverns for the loan of three stalactites for study. Brookhaven National Laboratory and Columbia University both made facilities available for this work.

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DISCUSSION

(speaker not identified) I can understand why one stalactite is a perfect crystal but I wonder why there isn't a gradation. For example, why couldn't a stalactite consist of two or more similarly oriented domains running the length of the stalactite?

W. A. BASSETT: I do find this. The soda straw may start out with four or more domains of calcite. Farther down the stalactite they gradually pinch out until only the most favorable domains remain. In some cases two domains will have a favorable orientation and you will find two domains extending from the top of the stalactite to the bottom side by side.

PAUL J. SHLICHTA, *Jet Propulsion Laboratory, California Institute of Technology*: Pursuing this a little bit further, there might be some question as to the lack of intermediate forms between the radial stalactite and the monocrystalline one.

BASSETT: I have an intermediate form here. It has a dozen or so randomly oriented zones on its surface. Apparently solution began to flow over the outside carrying in randomly oriented nuclei. In the course of time it would become a normal stalactite.

SHLICHTA: I would suggest that you would get the extreme case if complete drying took place at any stage of the game. You would then get a shell with randomly oriented crystals.

RANE L. CURL, *Shell Development Company*: Your first illustration shows a central dark zone in the hexagonal stalactite. This should mark the boundary of the original soda straw. If that ring marks a period of either drying or deposition of foreign matter on the surface, why would the hexagonal sheath maintain the original crystal orientation?

BASSETT: Even if it did undergo a period of drying, it doesn't necessarily mean a collecting of randomly oriented fragments on its surface. It could have dried completely with no formation of new calcite nuclei.

SHLICHTA: Is the black ring sharp?

BASSETT: It appears to be.

SHLICHTA: There are impurities which could collect in this central zone without nucleating new growth centers.

BASSETT: That is true. It might be a foreign dust on the surface.

RICHARD B. ANDERSON, *Bell Telephone Laboratories*: The Black Hills Caves are rather special. Most of the caves have large crystals in them. Rushmore Cave has more ordinary speleothems than any of the other caves. These peculiarities may have some effect.

BASSETT: It might be that either the impurities or the contaminations in the Pahasapa limestone are important.

GEORGE W. MOORE, *U. S. Geological Survey*: I think the crystals in the other caves are much older than the stalactites in Rushmore Cave. Obviously, Rushmore Cave speleothems are growing at the present time.

SHLICHTA: In the case of other hexagonal stalactites, are any of them found with natural terminations?

BASSETT: I have in this collection of soda straws, a specimen with partially developed hexagonal faces and a very nice scalenohedral termination.

MOORE: In Mayfield Cave, Texas, there was flooding with water after the deposition of ordinary stalactites. Many strange things happened. Many stalactites show crystal faces because of overgrowths. Some stalactites instead of being hexagonal have a rectangular cross-section.

WILLIAM E. MEYER, *Autonetics Division, N.A.A.*: You mentioned a specific set of conditions which you believe contributed to the formation of the hexagonal stalactite. Was there any evidence that other speleothems in the cave participated in these conditions. For example, do other stalactites show the black ring or any evidence for drying out?

BASSETT: We did not observe other stalactites with dark rings. Other speleothems may have experienced one or more of the unique conditions mentioned but a combination of the unique conditions would be required

for the formation of a hexagonal stalactite such as the one we have described.

MEYER: You have mentioned two or three conditions which would tend to produce hexagonal stalactites. Perhaps there is a fourth or fifth condition also necessary?

BASSETT: Perhaps one of the reasons that hexagonal stalactites are so rare is that people haven't been looking as hard for them as they might. This was driven home to me by this collection. Two of these soda straws have started to form hexagonal prism faces on their surfaces. The Rushmore Cave specimen may simply be an unusually well-developed one.

WILLIAM B. WHITE, *Pennsylvania State Uni-*

versity: I'd like to throw in one comment. Although the discussion has been limited to monocrystalline soda straw stalactites, one does observe rather massive, perhaps 2 x 8 inches, stalactites which break along a single cleavage plane and which show a characteristic rhombohedral fracture pattern on drying that indicates that the cleavage planes are indeed parallel throughout the length of the specimen. One also observes that these specimens are limited to caves which are well-sealed and very wet and humid where the growth processes are going on at full rate. Specific instances are the Guacharo Cave in Venezuela and McConnellstown Quarry Cave in Central Pennsylvania.

The Growth of Stalactites

by George W. Moore

ABSTRACT—Cave water is slightly acidic in the summer and slightly alkaline in the winter. Also, the carbon dioxide content of cave air is highest in the summer. These annual fluctuations result from seasonal variations in the production of carbon dioxide by microorganisms in the soil. Limestone is dissolved at the base of the soil zone in water rendered acidic by dissolved carbon dioxide and is deposited again when the soil water migrates downward into a cave and encounters the relatively low carbon dioxide content of the cave atmosphere. But the dissolving of the limestone is a slow process relative to the capacity of the water to dissolve. When the percolation of the water is also slow, stalactite growth is favored by the high concentrations of carbon dioxide produced in warm climates and during the warm season. When the percolation is fast under these conditions, however, the water will not be supersaturated when it reaches the stalactite, and growth cannot occur.

Water dripping from the tip of a stalactite deposits a central cylinder with vertical crystal orientation, whereas water flowing down the sides deposits radiating crystals. Stalactites on concrete structures have repeatedly given a false notion of the growth rate of cave stalactites, but radiocarbon dating, actual measurements in caves, and study of annual growth increments show that the rate of elongation, though variable, averages about a quarter of a millimeter a year.

INTRODUCTION

The origin of stalactites is a topic which has provoked thought since the earliest attempts to supply rational rather than magical explanations for natural phenomena. The term *stalactite* was first applied to pendant cave deposits in 1655 by the Danish naturalist Worm, but accurate observations and fairly reasonable interpretations had been offered much earlier. For example, the Roman scholar Pliny, writing at about the time of Christ, carefully described the growth of stalactites and stalagmites in caves in Italy, Greece, and Yugoslavia (Plinii, A.D. 77). Pliny recorded that the stalactites were formed by dripping water which had trickled down through the rocks. He suggested that they were formed when the water petrified or turned to stone.

During the Middle Ages, when science was eclipsed and the knowledge accumulated by the Greeks and Romans faded from memory, ideas on the growth of stalactites also were forgotten. During this period, people often turned to the Bible for answers to

such problems. The similarity of hundreds of stalactites hanging from the ceiling of a cave led some to propose that they all were specially created, each after its own kind.

Following the Renaissance, which marked the rebirth of the concept of explanation based on careful observation, the importance of dripping water to the origin of stalactites was rediscovered. In the writings of Gafarel (1650) and Plot (1677), accurate descriptions of the growth of stalactites are found, but in the absence of the modern theory of solutions, these writers were forced to retain the concept of Pliny put forth 15 centuries earlier—that stalactites result from the solidification of water. Subsequently, several additional concepts were proposed. One of the most interesting of these had its basis in the knowledge that when stalactites are broken, the colored growth layers resemble the growth rings of trees. This fact led Beaumont (1680) and de Tournefort (1718) to suggest that stalactites and stalagmites are "alive" and grow in the manner of plants.



Figure 1

Tubular stalactites in Table Mountain Cave, Wyoming (actual size).

When Lavoisier, in his classic paper on the true nature of water (1771), demonstrated that mineral deposits are formed by the deposition of material from solution, the groundwork was laid for modern ideas on the growth of stalactites. The theory of solutions led to the present concept that stalactites are formed from solutions saturated with respect to calcium carbonate, and from this fact consideration may be given to the details of the mechanism of stalactite growth.

SIZE AND SHAPE

True stalactites that have formed from dripping and downward-flowing water grow to massive proportions but have a lower size limit. This minimum size is equal to the diameter of a drop of water. The tips of conical stalactites ordinarily are not sharply pointed; they taper downward until their diameter is approximately 5 millimeters (the size of a drop), and at this point the smooth cone is abruptly truncated and provides a seat for the drops (fig. 1). This

truncation of the tips of conical stalactites supplies a clue to understanding an important relationship between the growth and internal structure of stalactites. Two somewhat different processes operate during the deposition of conical stalactites, and each of these processes controls a different part of the structure: (1) dripping water determines the hanging shape by depositing a small ring at the tip which encloses an unfilled central canal; and (2), all the remaining matter is deposited, not by dripping water, but by water flowing in a film down the outer surface (fig. 2).

When water moves only down the central canal of a stalactite, deposition does not occur on the outside of the stalactite, and the structure does not assume the characteristic conical shape. Stalactites formed in this way, when only the first of the two growth processes is operating, typically have tubular shapes. Some of the slender tubes reach lengths of a meter or more, and the longest example known is in Boranup Cave in western Australia (Robinson, 1960). It is 6.2 meters long and only 6 millimeters in diameter.

CRYSTAL ORIENTATION

Tubular stalactites have a different crystal arrangement than the outer parts of conical stalactites. The tubes and tube embryos at the center of large stalactites have structures in which the long axes of the calcite crystals are directed downward, whereas the outer part of a large stalactite possesses radiating crystals perpendicular to the axis of the stalactite (fig. 3). Tubular stalactites break along simple inclined cleavage planes reflecting their regular crystal orientation. Ordinarily the tube embryos can also be recognized in broken cross sections of larger stalactites by a marked contrast in angle between the cleavage planes of the outer part and a zone 5 millimeters in diameter at the center.

Rarely the normal growth of a tubular stalactite may be disturbed by flooding of the cave with water saturated with respect to calcium carbonate. When this happens, the round cross section of the tube, controlled by the shape of the drops, may develop crystal faces reflecting the true in-

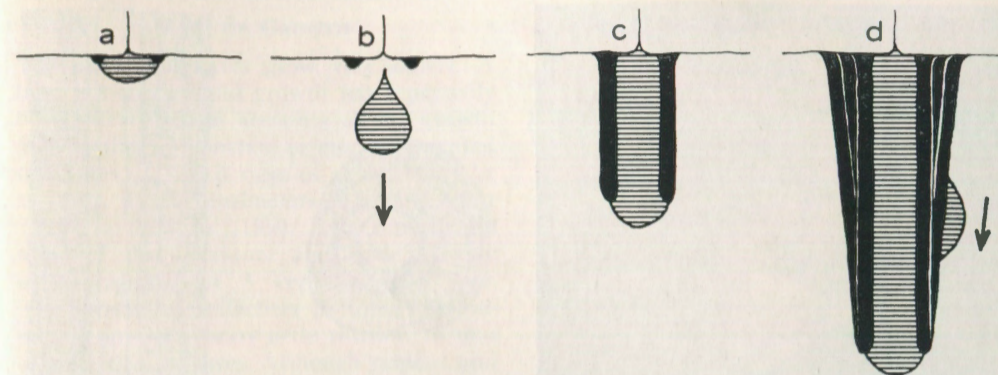


Figure 2

Development of a stalactite. (A-C) growth of a tube from dripping water; and (D) deposition of the outer layers from flowing water (twice actual size).

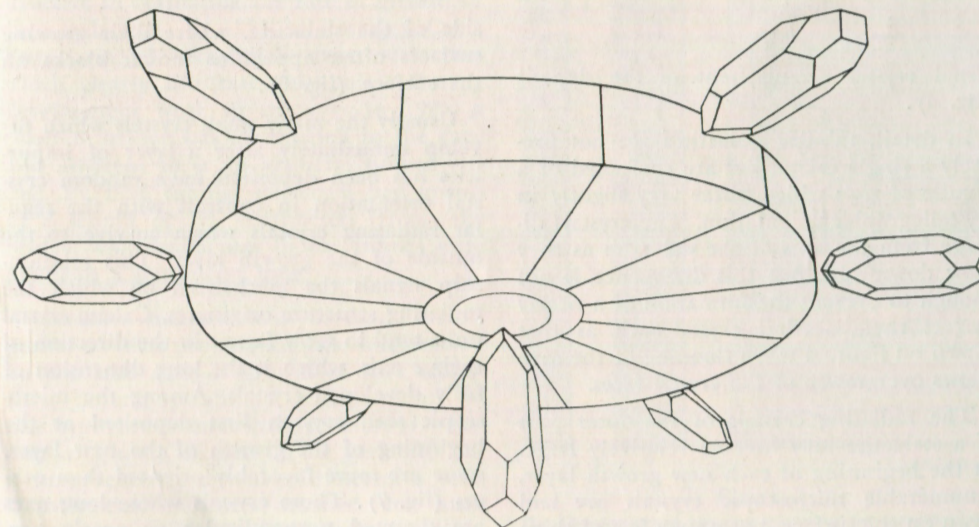


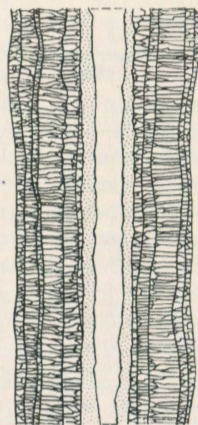
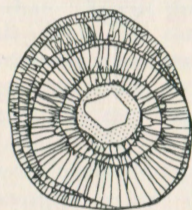
Figure 3

Crystal structure of a section of a conical stalactite showing radiating orientation in the outer layers and vertical orientation in the central tube embryo.



Figure 4

Rhombohedral calcite crystal which grew over a tubular stalactite in Rio Piedras Cave, Puerto Rico, when the cave passage was flooded (actual size).



10 millimeters

Figure 5

Crystal structure of a stalactite from Cumberland Bone Cave, Maryland, showing many small crystals at the inside of each growth layer which are survived by only a few at the outside of the layer. The central tube is dotted.

side of the stalactite, where their growing surfaces often appear as mosaic blocks on the surface (fig. 6).

Usually the many small crystals which develop immediately after a layer of impurities has been deposited have random crystal orientation in contrast with the regular radiating crystals which survive to the outside of the growth layer. This relationship signals the mechanism by which the radiating structure originates. Calcite crystal units tend to grow fastest in the direction of their *c* axis, which is the long dimension of fully developed crystals. Among the microscopic seed crystals first deposited at the beginning of the growth of the new layer, some are more favorably oriented than others (fig. 7). Those crystals whose long axes are directed perpendicular or nearly perpendicular to the growth surface tend to grow faster and larger, and they smother unfavorably oriented nearby seed crystals. Ultimately this selection process eliminates all crystals except those perfectly positioned with respect to the advancing surface of the stalactite.

RATE OF GROWTH

Stalactites in caves grow very slowly. A false notion of rapid growth has repeatedly been inferred from accounts of the growth of stalactites on concrete or mortar-cemented structures on which rates of growth may be as much as 10 centimeters a year. Fischer (1934) and Hicks (1950) have summarized some of this literature and find the rate to average about 3 centimeters a year. The growth of stalactites in these environments, however, bears little relation to that of stalactites in caves. Although cement and mortar are made from limestone, they have been altered by roasting during which carbon dioxide was driven off. When water is added to cement or mortar, calcium hydroxide is produced along with other products. Calcium hydroxide is approximately 100 times more soluble in water than calcium carbonate, and a solution containing it may combine rapidly with carbon dioxide from the atmosphere to produce fast-growing stalactites. Hence, stalactites formed by solutions from these materials are not instructive in evaluating the rate of growth of cave stalactites. In 1956 in Postojna Cave, Yugoslavia, I examined some stalactites which clearly illustrate this point. During development work in the cave in 1925, a concrete bridge was constructed in the cave and adjacent to it an artificial tunnel was dug. By 1956 tubular stalactites had grown to a length of 50 centimeters from the bridge, while stalactites in the tunnel were less than a centimeter long.

Successive measurements in caves over a period of years provide the best information on the true rate of growth of cave stalactites. Several published measurements of this type are summarized in table 1. The rate of growth is seen to be variable, but it never exceeds several millimeters a year. Usually the stalactites selected for such growth-rate studies are especially fast-growing individuals. Numerous other unpublished observations by tourist cave operators suggest that the average rate of stalactite elongation is about a quarter of a millimeter a year.

Recently the radiocarbon method has been employed to determine the rate of

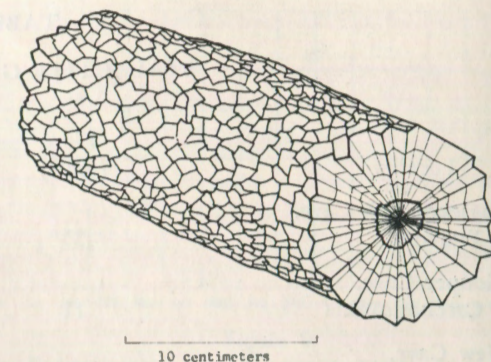


Figure 6

Radiating crystals in a stalactite from Gaucharo Cave, Venezuela, showing the mosaic formed by the ends of the crystal pyramids on the surface (drawing by John Haas).

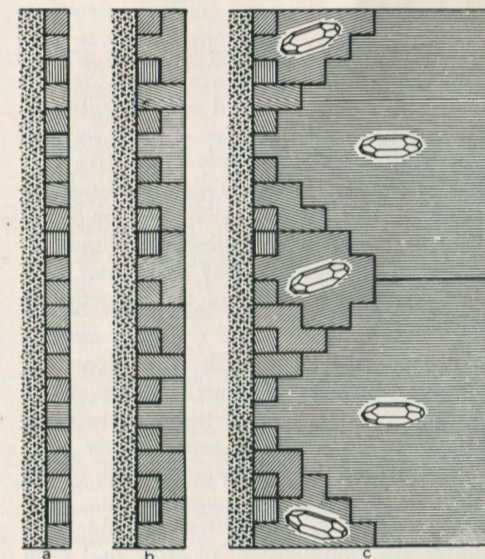


Figure 7

Development of crystal orientation perpendicular to the advancing surface of a stalactite: (a) initial deposition of randomly oriented seed crystals on a layer of impurities (dotted pattern); (b) defeat by crowding of crystals whose direction of fastest growth (line direction on pattern) is far from perpendicular to the surface; and (c) ultimate survival only of crystals whose long axes are perpendicular.

TABLE 1
STALACTITE GROWTH RATE

Locality	Time (years)	Growth (millimeters)	Rate (millimeters per year)	Reference
Ingleborough Cave, England	35	1-6	0.03-0.17	Dawkins, 1874
Slouper Cave, Czechoslovakia	11	30-40	2.7-3.6	Kríz, 1892
New Cave, Ireland	36	80	2.2	Coleman, 1945

thickening of a stalagmitic cave deposit in Moaning Cave, California (Broecker and others, 1960). The radiocarbon dating indicated that 8.8 centimeters of this material formed in approximately 1,400 years—equal in this case to only 0.06 millimeters per year.

Another way of studying stalactite growth is by examining the growth layers. Several investigators have worked with the brown growth rings which appear in cross sections of stalactites and look very much like tree rings (Vitasec, 1940). One handicap to studies of this kind is that the rings are usually incomplete, as shown on figure 5, because of the variable way that water runs down on different sides of the stalactite at various times.

Another type of growth line occurs on the outer surfaces of some tubular stalactites (fig. 8); this type of line may be more uniform and preserve a more nearly complete record of the downward growth of the stalactite than the concentric rings. The lines on tubular stalactites resemble the grooves on phonograph records, and each line may represent one year. These lines probably result from the fact that during the wet and dry seasons of the year the stalactites grow at different rates. The section of a tubular stalactite from Soldiers Cave, California, shown on figure 8, is 18 millimeters long and has 89 growth rings. If the rings are assumed to be annual, a growth rate of 0.2 millimeters per year is indicated—a value that is compatible with

the other methods of estimating growth-rate. The variation of thickness exhibited by the growth increments of tubular stalactites possibly records variation in rainfall or the level of the water table in the area of the cave, but these factors have not been investigated further.

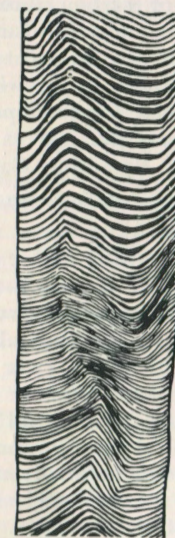
MECHANISM OF GROWTH

Factors governing the growth of stalactites that might first come to mind are the rate of water flow and the rate of evaporation. But the growth rate is not necessarily proportional to the rate of flow because, if the water is undersaturated with respect to calcium carbonate, calcite cannot be deposited. Moreover, the air of most caves is saturated with water vapor, so evaporation of water ordinarily is impossible. Deposition is caused chiefly by a change in calcite solubility which accompanies loss of carbon dioxide gas from the dripping water.

The carbon dioxide content of water is controlled principally by the percent of carbon dioxide in the air to which the solution has been exposed. The surface atmosphere has a carbon dioxide content of only 0.03 per cent, so the contribution of atmospheric carbon dioxide to cave origin or stalactite growth is negligible. The partial pressure of carbon dioxide in soil air, however, is commonly more than 10 percent (Coleman and Mehlich, 1957), and this soil carbon dioxide is dissolved in water and carried down into the cave. It subsequently leaves the dripping water in the cave when

the low carbon dioxide partial pressure of the cave atmosphere is encountered and causes calcite to be deposited.

Radiocarbon analysis of stalactitic material, in addition to supplying a precise measure of the rate of growth, also contributes information on the mechanism of growth. The dating of stalactites by the radiocarbon method depends on the facts that carbon-14 produced in the atmosphere has a relatively short half-life and that it finds its way into stalactites. The limestone is sufficiently old that radio-carbon once present in it has now completely decayed. According to the usual interpretation, one molecule of carbon dioxide from decaying soil vegetation (rich in radiocarbon) combines with water and one molecule of calcium carbonate from the limestone (free of radiocarbon) to produce two bicarbonate ions. When this bicarbonate enters the cave and loses carbon dioxide to produce a stalactite, one might expect that the radiocarbon content of the stalactite would be only 50 percent that of the decaying vegetation. It turns out, however, that presently grow-



10 millimeters

Figure 8

Growth increments on the outer surface of a tubular stalactite from Soldiers Cave, California.

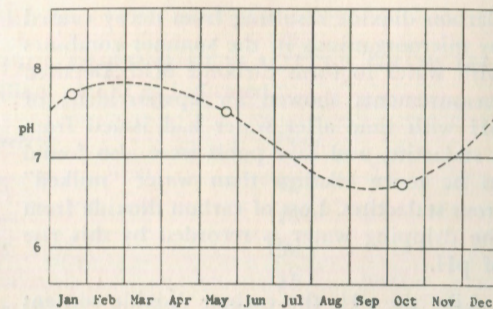


Figure 9

Determinations of pH during 1958 in Gage Caverns, New York, and a hypothetical curve of annual fluctuation.

ing stalactites contain about 90 percent of the radiocarbon content of modern vegetation (Broecker and others, 1960). This means that after the limestone is dissolved at the base of the soil zone, the calcium bicarbonate remains in contact with the reservoir of carbon dioxide in the soil long enough for the abundant radiocarbon-bearing soil bicarbonate to exchange with and nearly mask the small quantity of available bicarbonate from the limestone before the solution moves down through the rock to the cave. The radiocarbon evidence suggests that very little dissolving of radiocarbon-free limestone occurs after the water leaves the soil zone, and that the water is transmitted essentially unchanged to its underground outlet.

In order to ascertain whether or not a variation in the acidity of stalactite water occurs during the year, such as might indicate that stalactites grow more rapidly in one season than in another, pH measurements were made in January, May, and October in Gage Caverns, New York. The results from Gage Caverns (fig. 9) along with measurements in other caves given below show that a significant variation in the pH of cave water takes place throughout the year. The water is slightly alkaline in the winter and slightly acid in the summer.

The annual cycle of pH variation probably results from the activity of microorganisms in the soil whose life processes are most vigorous during warm parts of the year.

Carbon dioxide resulting from decay caused by microorganisms in the summer combines with water to form carbonic acid. Detailed measurements showed an upward drift of pH with time after water had issued from a stalactite, and cave pools were also found to be more alkaline than water "milked" from stalactites. Loss of carbon dioxide from the dripping water is recorded by this rise of pH.

Like the pH, the carbon dioxide content of cave air undergoes an annual fluctuation related to the carbon dioxide production of soil microorganisms. Analyses by Shinya Oana (oral communication, 1958) of air samples from Breathing Cave, Virginia, collected on January 1 and May 25, 1958, were respectively 0.037 and 0.071 percent. The January value is only slightly above that of the normal surface atmosphere, whereas the May value is twice that of the surface, showing that by May carbon dioxide is being pumped vigorously into the cave. Stalactite growth probably is virtually arrested during the winter, and the principal lengthening occurs during the warm months.

As first pointed out in Europe by Corbel (1952), the size of stalactites is related to the latitude of their caves. In the southern United States, cave deposits are very massive; in New England, their size is modest; and Arctic caves lack stalactites entirely. To study this latitude effect further, the pH of water dripping from similar tubular stalactites in three caves spaced four degrees of latitude apart was measured between May 22 and May 26, 1958. Stalactite water in Gage Caverns, New York, had a pH of 7.5; Breathing Cave, Virginia, 6.5; and Tumbling Rock Cave, Alabama, 5.8. These results illustrate the lower pH caused by greater production of carbon dioxide in soils overlying southern caves during the warm season.

The pH of water from the same caves was tested in the winter between December 30, 1957, and January 18, 1958. The results are as follows: Gage Caverns, 7.7; Breathing Cave, 8.1; and Tumbling Rock Cave, 8.2. In the winter the water from all the caves was quite alkaline, indicating that little decay was occurring in the overlying soil.

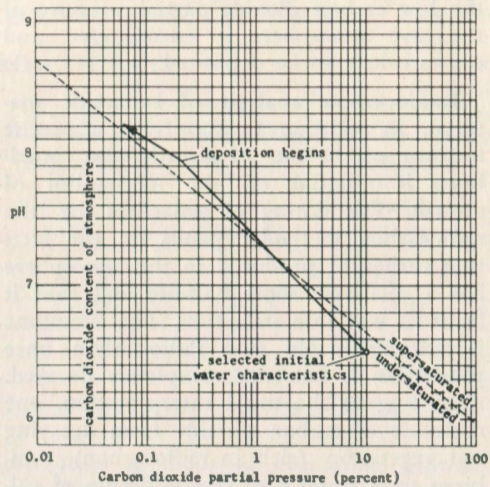


Figure 10
Changes which occur immediately after water enters a cave and during subsequent deposition of calcite on a stalactite (dashed equilibrium line plotted from Garrels, 1960, p. 50).

The slightly lower pH found in the northern caves could have resulted from the greater solubility of carbon dioxide in colder water. In the summer this factor is believed to be overridden by the greater carbon dioxide production, but in the winter it may assume dominance. Cave temperature is constant throughout the year as follows: Gage Caverns, 8°C; Breathing Cave, 11°C; and Tumbling Rock Cave, 14°C.

The changes which occur when water issues from the ceiling of a cave and begins to deposit calcite during the active stalactite-growing season are shown diagrammatically on figure 10. A general case has been selected in which the water had been exposed to a partial pressure of 10 percent carbon dioxide in the soil and did not achieve chemical equilibrium with respect to the limestone before it moved through the rock to the cave. The water with a selected pH of 6.5, therefore, enters the cave in an undersaturated state. Carbon dioxide is given off immediately when the water meets the low partial pressure of the cave atmosphere, and pH rises with the loss of carbon dioxide. The selected solution reaches equilibrium with calcite at a carbon

TABLE 2
CHANGES IN WATER CHARACTERISTICS DURING STALACTITE GROWTH
(Analyses in parts per million, except as indicated.)

	Stalactite	Pool
Ca	95	42
Mg	—	18
HCO ₃	348	190
SO ₄	—	15
CO ₂ (percent)	1.8	—
pH	7.30	7.99

dioxide partial pressure of 1.3 percent and a pH of about 7.2. Ordinarily, deposition does not commence immediately, and the solution attains a measure of supersaturation before deposition occurs on the pre-existing stalactite nucleus. A long period of deposition then follows as the carbon dioxide content of the water slowly adjusts itself to that of the cave atmosphere. Calcite is deposited first on the stalactite, then on the stalagmite, and finally the water may join a cave stream and deposit a rimstone dam across its course. Ordinarily, by the time the water returns to the ground surface from a spring, the carbon dioxide in solution has attained equilibrium with the atmosphere, and all the available calcium carbonate has been precipitated.

A tubular stalactite and a small crystallized pool which directly underlies it were studied in Cave City Cave, California. Samples were collected from the stalactite during the first week of November by inserting a hypodermic needle approximately 3 centimeters into the tube from below and slowly filling the syringe at precisely the rate of water flow. The calcium, bicarbonate, carbon dioxide, and pH were determined within an hour in a laboratory truck at the cave, and the magnesium and sulfate content of the pool water were analysed later. The partial pressure of carbon dioxide was measured with an apparatus described by Severinghaus and Bradley (1958) which was originally designed for blood-gas analysis. The results are given in table 2, with the temperature-dependent properties quoted at 20°C.

Water dripped from the stalactite once every 23 seconds, and its flow was 30 milliliters per hour. The cave air temperature was 12.7°C and the relative humidity, 100 percent.

When plotted on figure 10, the pH and carbon dioxide partial pressure in the stalactite indicate that the water there was supersaturated with respect to calcite. This is supported by the fact that recently formed calcite cave rafts were floating on the pool and that the calcium and bicarbonate content decrease in the pool water relative to that in the stalactite. As the rate of flow from the stalactite was known, and no other stalactites supply this small pool, the decrease was used to calculate the rate of deposition of calcite. The rate determined from this data proved to be 0.014 grams per day. Only a small percent was probably deposited on the stalactite, however, and the remainder of the calcite formed on the walls and surface of the pool.

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DISCUSSION

JOHN R. DUNNING, JR., *Yale University*: Do southern caves contain fewer speleothems because more microorganisms are present in the overlying soil?

MOORE: It turns out that southern caves have much larger speleothems. On the other hand, in the Arctic, caves generally lack stalactites. I didn't go into the role of microorganisms today, but obviously they are very important. They could provide an alternative explanation for the development of crystal structure which I outlined. It is usually the low temperature minerals that have radial crystal structure, and even unusual minerals such as malachite may be helped in their crystallization by microorganisms. I think that microorganisms living in warm southern caves are the most important factor in developing the large stalagmites there. Bacterial action in southern caves causes precipitation from supersaturated solutions that, in northern caves, would simply remain supersaturated.

STANDIFORD GORIN, *Cumberland Caverns*: Wouldn't the rate of evaporation of solutions and the concentration of carbonate contribute to the rate of growth?

MOORE: Evaporation is quite unimportant, because of the high humidity of caves. Loss of carbon dioxide is almost all-important.

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although in dry caves evaporation could play a part. My measurements of pH don't tell as much as they might. It would be much better to know the actual concentration of calcium carbonate and bicarbonate in solution. This should be done—especially in a single cave, on a single stalactite, at regular intervals over a year.

RANE L. CURL, *Shell Development Co.*: First, a comment on the previous question on northern and southern caves. I would expect that in southern caves, the water dripping into the cave to form the deposits would have a larger content of mineral matter in it because of the greater availability of carbon dioxide at the surface. Secondly, you say that stalactites measured by carbon-14 methods contain 80 percent recent carbon. Is this true for all the carbonate in the stalactite?

MOORE: Only the outer layers.

CURL: I didn't quite catch your explanation. In theory, 50 percent of the carbonate should come from the air, and 50 percent from the rock, giving 50 percent of the actual age.

MOORE: The explanation is that the process takes place at the upper surface of the limestone where the rock is in direct contact with the soil. After the limestone goes into

solution, the solution remains in contact with the soil long enough for equilibrium to be obtained between the carbon-isotope ratio in the water and the ratio in the soil thus destroying the "old age" of the carbon from the limestone.

CURL: You are exchanging zero-age carbon with infinite-age carbon?

MOORE: Yes, thereby moving the final ratio from 50 to 90 percent modern carbon.

CURL: I have observed, in the center of broken stalactites, pure white chunky calcite crystals with all the appearance of later deposition. Is this recrystallization?

MOORE: No. It is deposition within the central tube.

CURL: This opening extends half an inch or so.

MOORE: If it is really half an inch, it is larger than the average tubular stalactite. Quite often the deposition in the central canal follows the crystal lattice of the tube. Then a zone with the same crystal orientation as the tube forms, usually about half a centimeter in diameter. The central canal is even smaller than this. I find it hard to imagine randomly-oriented crystals more than four millimeters in diameter in the center.

CURL: I have seen sections of stalagmites where an aragonite stalagmite appeared to be recrystallizing to massive calcite. All I observed was the mosaic structure. I did not check the orientation of the crystals.

MOORE: Of course stalagmites are an entirely different story. They are formed by flowing water rather than from a hanging drop. The central part of stalactite is the only part formed by dripping. The outer part of a stalactite is formed in the same manner as stalagmite. I'm sorry I implied that recrystallization never occurs in stalactites. I've seen aragonite stalactites and stalagmites that have partly transformed into calcite. I was really only referring to calcite deposits.

CURL: Concerning a stalactitic form, the drapery, I have observed that draperies consist of calcite mosaic rods up to two feet in

length. They are approximately the size of a hemispherical drop of water that could hang from a rod of the same diameter. These are precipitated externally. Why does this system maintain itself so nicely? It has a very intricate structure.

MOORE: I'll start by saying that a drapery is a flowing-water deposit, not a dripping water deposit. The water flows along a sinuous course on the bottom of the drapery. Every once in a while a layer of impurities causes a break in deposition, and crystal growth must start over again. At first the small new crystals are randomly oriented. Soon, however, they tend to orient in the direction of freedom which is downward. I think they could obtain almost any size, although they are commonly equidimensional, and the drapery maintains a constant width and has crystals all the same size perpendicular to the course of water flow.

JOHN A. STELLMACK, *Pennsylvania State University*: I was just wondering if anyone has ever dated the carbon dioxide in a cave atmosphere by the radiocarbon method?

MOORE: A man in Romania measured radioactivity with an electroscope [G. Atanasiu, 1958, Acad. rep. populare Romine Studii cercetari fiz., v. 9, p. 313-316]. No detailed work has been done. Shinya Oana and I did some work on the stable isotopes of carbon in the atmosphere of Gage Caverns, N. Y., and, for what it's worth, the delta-value ratio is about -19.

STELLMACK: Wouldn't the cavers themselves contaminate the cave air?

MOORE: Yes. The acetylene from carbide lamps has a delta value of about -25. The human breath is about -21. All these things are operating in exactly the direction to confuse us most as the soil carbon dioxide is about -25 and the surface atmosphere is about -8. It's best to use a clean cave if you can.

PAUL J. SCHLICHTA, *Jet Propulsion Laboratory, California Institute of Technology*: Can you tell me what minerals occur as stalactites?

MOORE: Many minerals have been observed as stalactites but not too many in caves. There is a paper on this in the National Speleological Society Bulletin [F. L. Hicks, 1950, v. 12, p. 63-72] that completely reviews all stalactitic minerals. It is not as useful to the speleologist as it first appears because it lists every mineral that appears in stalactitic form. The minerals that I can think of that occur as stalactites in caves are malachite, aragonite, calcite, ice, goethite, and gypsum.

WILLIAM E. DAVIES, *U. S. Geological Survey*: There is a rare one in Shenandoah Caverns, Virginia. It is a stalactite made of pitch. STELLMACK: I have seen calcium hydroxide stalactites growing from a dump of carbide from lamps.

MOORE: I have recently been preparing a list of cave minerals but haven't limited it to stalactites, as usually the rare minerals occur in other forms.

EUGENE P. VEHS�AGE, *Great Neck, N. Y.*: You mentioned the rate of growth of stalactites as one inch per hundred years. Is this a linear inch or a cubic inch?

MOORE: It is a linear inch. I'm sorry I didn't emphasize that point. Many commercial cave guides tell you it is a cubic inch. This is nonsense. Usually they point to some large stalagmite that might be five or six feet in diameter with perhaps 100 small stalactites over it. That stalagmite is growing fast, but another next to it, with a diameter of one inch and only a single stalactite over it, is growing quite slowly in terms of cubic inches a year.

BULLETIN

of

THE NATIONAL SPELEOLOGICAL SOCIETY

VOLUME 24

1962

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