

The Aragonite-Calcite Problem

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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), Pobeguain (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. Pobeguin (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.).

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, Sohn (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 nowhere 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 Pobeguain (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), Pobeguain 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 finely 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-Duffy, 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-

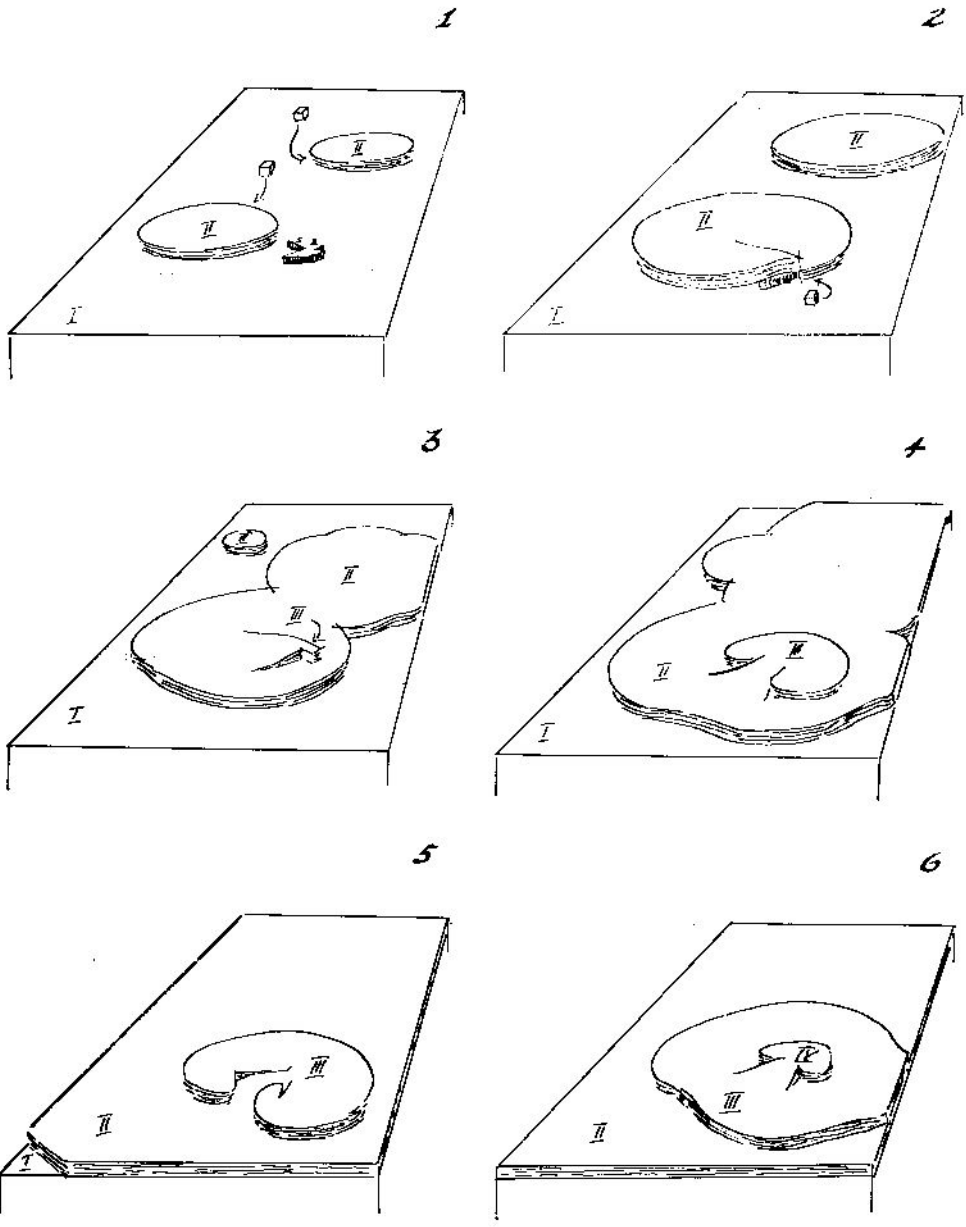


Figure 1-6

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 ratio 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 ratio 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^{1-} ; $(\text{PO}_3)_0^{0-}$; 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

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.