

IV.—*On some Artificial Forms of Silica, illustrative of the structure of Agates, Chalcedonies, &c.*

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(Read September 2nd, 1881.)

IT is a common chemical fact, that when a solution containing an alkaline silicate is acted upon by any reagent capable of separating the silica from the base, the silica is in the majority of cases thrown down in a solid form. The fact of this reaction is all that, as a rule, the chemist would look at: but in addition to the mere chemical fact of the precipitation of the silica, another most important element from the mineralogist's point of view is that of the *form* in which this precipitate of solid matter appears. This form naturally varies with the various conditions of the experiment, and it is by the study of these varying forms that the authors have sought to elucidate, experimentally, the wondrous and beautiful varieties of structure which are so familiar to us in the endless forms of silica occurring in nature.

The infinite variety in the great group of banded agates falls readily into two types. The *first* in which the solidification appears to have taken place in successive layers from within *outwards*; and the *second*, in which the impression is conveyed that the order of growth has been from without *inwards*.

In both cases, beyond the successive bandings there is very frequently observed a crystalline mass of silica, which does not present the banded structure.

In the first class this crystalline mass is to the *outside* of the banded part; in the second, it is towards the *inside*, as though there had been a central cavity within the bands which had become filled with crystalline unbanded silica.

Assuming, for the convenience of nomenclature, that these two types are the results of the two methods of growth indicated—a view we hope to justify in the course of this paper—we may name these the *exogenous* and *endogenous* types respectively.

With the exogenous type of agate are grouped such stalactitic forms of silica as show in transverse section a series of concentric rings or bands: and a careful examination of cut stones of this class

will shew the extreme frequency of the occurrence of these stalactitic forms in agate structure, more especially when such structure is intimately examined in microscopic sections. The last layers of a portion shewing exogenous growth frequently become the first of an adjoining portion, whose growth structure falls under the endogenous type.

The unbanded and mossy types, occurring in such stones as jaspers and moss-agates, form a separate group, of which we shall have something to say further on.

Let us now first take the *exogenous* or stalactitic type, and seek by experiment to elucidate its genesis and structure.

We may get stalactitic forms of silica by taking a solution of silicate of potash or soda, and dropping into it; or allowing to run down the sides of the containing vessel, any of the strong acids; but in order to get the best results and to produce the beautiful branching coral-like forms, our mode of procedure is as follows.

A strong solution of silicate is taken containing a certain amount of alkaline carbonate, and a strong acid (sulphuric seems to give the best results) is introduced by means of a pipette to the bottom of the vessel in which the solution is contained.

Bubbles of carbonic acid gas immediately arise, carrying with them a certain amount of the stronger acid. Round the stream of ascending bubbles, silica is deposited by the decomposition of the alkaline silicate, and in a very few minutes a tube is formed reaching from the bottom to the surface of the solution.

This tube is at first very thin, and through its walls the ascending acid continues to act upon the surrounding silicate, the walls of the tube in consequence constantly growing in thickness by the deposition of additional silica on its outer surface. As long as the flow of acid is kept up, so long does the tube grow in diameter by the deposit of successive layers, and the result is a hollow stalactite ringed in cross section.*

The carbonic acid evolved from the carbonate in the solution is essential to the successful commencement of the tube, but when this is once formed, the sulphuric or other acid can be itself forced through it, and by the application of pressure to the surface of the fluid in the pipette, the action can be kept up for a long time, and stalactites of $\frac{3}{4}$ inch in diameter can be formed with little difficulty. The same result can be produced by passing an acid gas, or even air highly

* Plate 1, Fig. 1. shews a group of such stalactitic growths of silica. At A and B these have come in contact with the sides of the containing vessel, and have thus been made, as it were, in section, shewing their hollow nature.

charged with an acid, through the alkaline silicate solution, and it will easily be seen that analogous effects can be produced by the action of any other reagents capable of separating the silica, such as acid salts of various metals. In fact the process can be varied in a hundred different ways. In natural siliceous stones where stalactitic forms enter into the structure, we constantly observe a central core, frequently of iron or other oxide, which appears to represent the original tube which has subsequently been filled up, whilst sometimes the cavity remains more or less completely as such. These stalactites of course do not grow up by any means in constantly straight regular forms, but assume irregular and branched ones, more like those of coral than anything else, according to the direction in which the bubbles of gas or the acid escapes from the end, or from points of least resistance in the sides, of the tube. Glauber's "Iron tree" is one form of this stalactitic growth.

The specific gravity of the fluid in which the stalactites are made, as compared with those of the reagent employed and of the precipitated silica, has of course much to do with the form assumed. Where these are equal, the tubes may take indifferently any direction with regard to gravity—and this is precisely what we find in nature, where it sometimes appears as if gravity had not had much to do with the directions assumed.

We consider then that the stalactitic productions thus made are the analogues of all the group of banded stalactitic growths which enter so largely into the constitution of many siliceous stones, where the growth appears to have proceeded from a central cavity, now frequently only a core, by reason of subsequent filling in.

If the action is carried so far that the surrounding fluid becomes saturated with acid reagent, the whole of this surrounding fluid gelatinizes by the precipitation of amorphous gelatinous silica, and if we suppose a case in which such stalactitic forms have been produced in nature in an enclosed rock cavity containing an alkaline silicate solution, by the infiltration of an acid solution, a like result would occur. In point of fact, as we have already stated, such natural forms constantly occur with a surrounding mass of crystallized un-banded silica, and this we are led by many observations to regard as the analogue in nature of the gelatinous silica resulting from the saturation of the fluid in which the stalactites have been formed. Whether in nature this crystalline silica has been originally deposited in a gelatinous form, and subsequently crystallised, is a little out of the scope of this paper: but analogy leads us to regard this as most probable.

II. We come now to the question of the formation of banded agates of what we have called the *endogenous* type; which are in reality, so to speak, the converse of the type of structure which we have just been considering.

Assuming hypothetically a rock cavity containing a solution of alkaline silicate, and the rock in which this cavity is situated permeated with an acid solution or gas, we should naturally expect to find a layer of silica deposited on the walls of such a cavity, and as the action continued more and more silica would be deposited; and if the solution were *enclosed* in the rock cavity, the central portion would, when the action had continued to a certain point, set in an amorphous mass.

This action is very completely paralleled in some of the preparations which we have made, and in some of these we have found that a central vacant space was left, owing to there not being enough silica in the solution to fill the whole cavity when precipitated in the gelatinous form. This is precisely what occurs in many natural agates, where we find a deposit of crystalline unbanded silica within the banded portion, with a vacant space in the centre of all.

We have, so far, dealt only with the production of these various forms in more or less pure silica: but by the use of acid solutions containing various metallic and earthy salts, we can imitate, to a great extent, the colouring of natural stones. More especially is this the case in the next group with which we have to deal.

Jaspers, Moss-agates, &c. The varieties of structure of the class of stones roughly grouped as above, are exceedingly interesting and beautiful. The way in which the various colouring matters are arranged, suggests at once the idea of *chemical precipitates*, and although, perhaps, the different types of structure are not so strongly marked as in those groups with which we have already dealt, yet there is much of interest in their elucidation.

Perhaps the most prevalent colouring matters in this class of stone are the red and yellow ferric and the green ferrous oxides. Both these classes may be readily imitated by introducing into alkaline silicates various ferric and ferrous salts. If an acid solution of a ferric salt—for instance ferric chloride—be so introduced, we find, first, a more or less flocculent precipitate coloured red or yellowish; and subsequently, as the action goes on, around this grows a filmy white deposit of silica, which frequently falls into banded forms, precisely analogous to constantly recurring markings in jaspers and allied stones. With ferrous salts, again, the green mossy markings of the moss-agate and the darker colour of the onyx can be perfectly produced.

Many interesting forms can be obtained by allowing stalactitic forms to come in contact, as they grow, with the sides of the containing vessel, by which means they may be made, as it were, in section, and the progress of their growth readily and conveniently watched. By combinations of these methods, a vessel may be entirely filled up with different forms of structure and colouring, presenting a very close resemblance to the natural products whose genesis it is sought to illustrate.*

It would be impossible within the compass of a paper of any reasonable length to go into all the variety of solutions and reagents with which we have worked, or to give all the special coincidences with natural form and structure which we have observed; but the following brief notes of some such special points may be of interest.

Horizontal banding is frequently met with in natural agates, and we have found it very completely reproduced in many of our preparations.

Some alkaline silicate was poured into a dilute solution of silicate of soda, which had been previously acidulated with dilute hydrochloric acid. A jelly was at once formed, enclosing in a species of cavity a portion of the alkaline solution. Into this the hydrochloric acid, together with the chloride of sodium resulting from the decomposition of the silicate, exuded from the gelatinous mass, and a series of horizontal bands extending across the cavity gradually formed.†

A solution of commercial alkaline silicate, particularly silicate of soda, is capable of dissolving considerable quantities both of pure gelatinous silica, and also of various silicates, such as those formed by precipitation with sulphates of copper and iron, as well as those of the alkaline earths.

In watching the growth of these stalactitic accretions in section on the sides of the containing vessel, the production of the bands has been observed to vary with different conditions of—1st, temperature, 2nd, acidity of precipitating solutions, 3rd, pressure.

If a solution of ferric sulphate, ferric chloride, or cupric sulphate, be poured into an alkaline silicate, coloured precipitates result, which, when washed, we have dissolved in alkaline silicates, producing the

* Plate II shows two examples of this. In both preparations the growth has commenced by stalactitic forms coming in contact with the sides of the containing vessel, and by continuing the action these have developed a series of successive bands external to the original tubes. The space beyond these bands consists of almost structureless silica due to the ultimate saturation of the alkaline silicate with the acid reagent.

† Plate III, fig. 1.

purplish red and green solutions exhibited, by the use of which in our preparations we have found the various colours of natural stones very closely imitated.

Hair-like Enclosures in Silica.—To produce the specimens figured in Plate III, fig. 2, the following process was adopted. A solution of silicate of soda, containing carbonate of soda, was taken; at the bottom of the vessel small fragments of acid salts, such as ferrous and ferric sulphates, were placed. The action of these on the carbonate in the solution gave rise to very minute bubbles. These ascending through the solution were followed by others, till a tube was formed reaching often to the top of the alkaline liquid. In the reaction between the iron salt and the solution, the tube became filled with a ferruginous liquid, and thereby coloured red, brown, or black, according to the substances employed.

So-called "Orifices of Inlet."—When the continuity of the bands is interrupted by the escape from within the cavity which they surround of the contained acid solution or gas, an appearance results closely resembling the so-called "Orifices of Inlet" in natural agates. The bands are bent outwards and thinned away at their interrupted ends, and at times the space between them is filled with a tubular stalactitic form, as shewn in Plate 1, fig. 2. Our observations and experiments enable us fully to confirm the view of those who hold that these so-called "Orifices of Inlet" are in reality more or less complete efforts to form outlets.

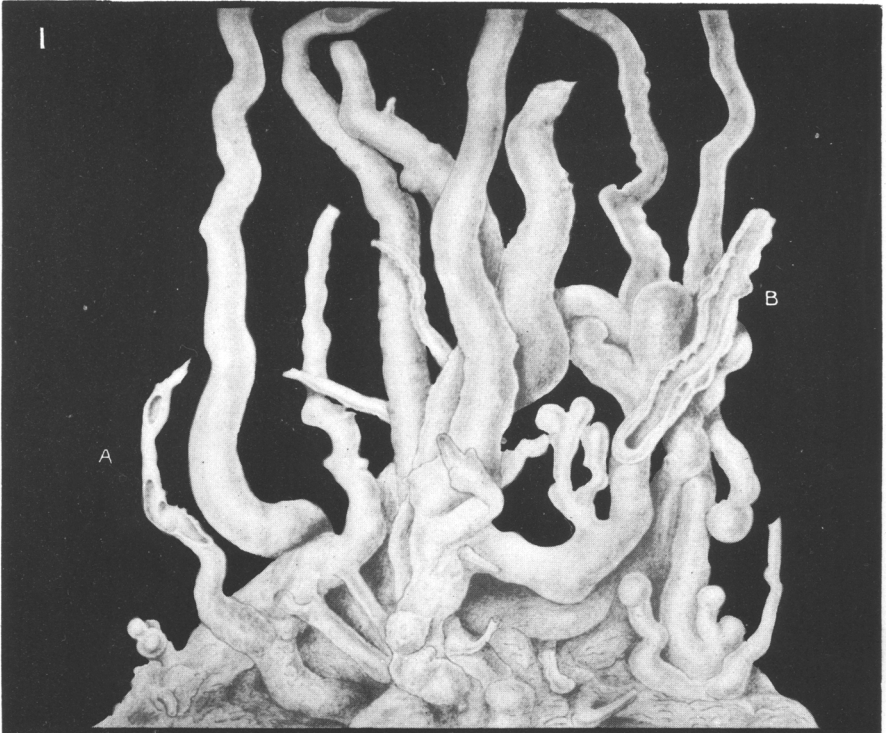
The precipitated silica in these preparations, being deposited at no great pressure or temperature, of course falls far short of a perfect reproduction of the natural stone in point of hardness and stability. Exposed to the air they, for the most part, dry up and crumble away, although we have produced some forms which approximate closely to common opal in appearance, though of lower specific gravity, and these remain with little or no alteration after once being dried. It is only in form and structure that we can as yet claim to produce any imitation of nature's products: but it is conceivable that under suitable conditions of heat and pressure closer imitations might be made.

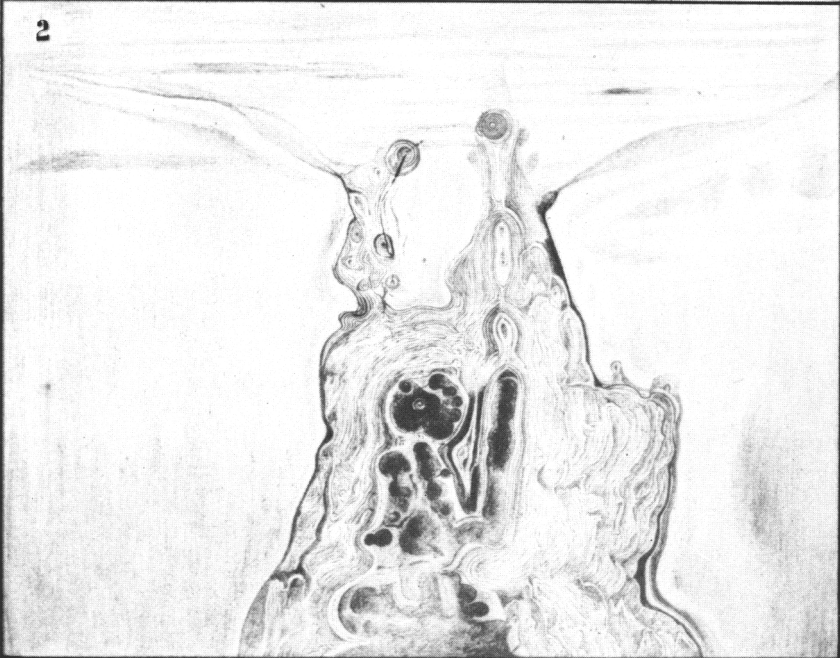
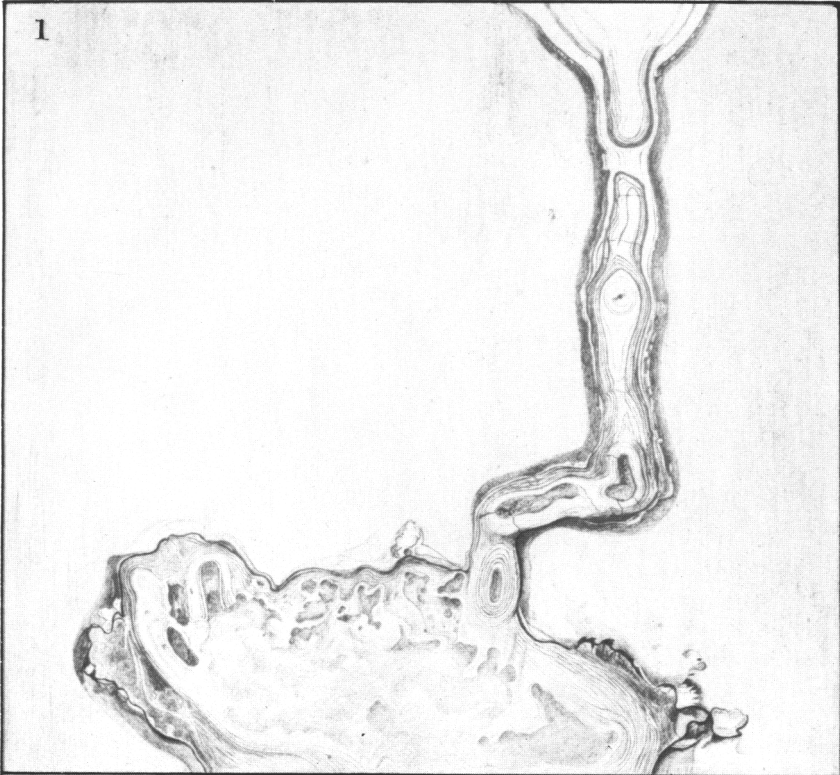
How far in nature the assumption of a crystalline structure may have taken place subsequently to the original solidification, is a question upon which, so far, we can only speculate; but we think it is probable that this may, to a great extent, have been the case. We do not touch upon this point in other than a tentative sense, in the hopes of eliciting from others any evidence which they may be able to offer on the point.

In conclusion, we have to acknowledge our indebtedness to Messrs. Goosage, of Widnes, for very kindly and generously placing at our disposal the material necessary for these experiments.

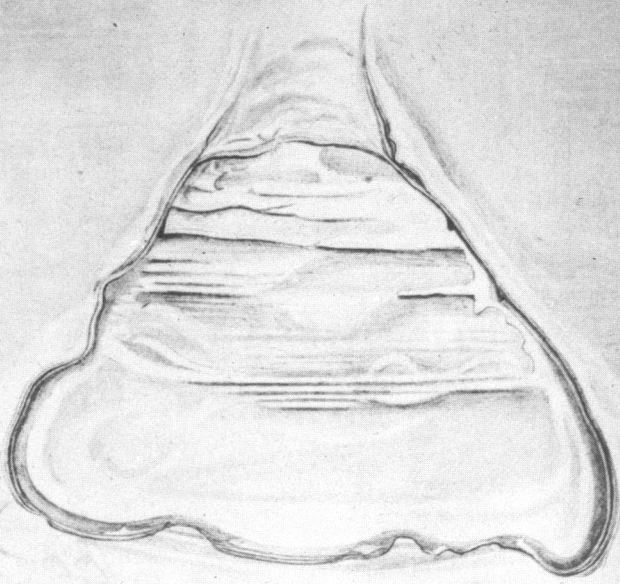
Mr. Wm. Lant Carpenter (B.A., B.Sc., F.C.S.) as a visitor, but as a late manufacturer of silicate of soda, begged to congratulate the authors upon their very admirable paper, and to offer two remarks thereon. The authors had been unable to obtain specimens of precipitated silica possessing any degree of hardness, most of them drying up and crumbling. About 15 years ago he had had occasion to prepare, on a large scale, great quantities of precipitated hydrated silica, by decomposing solutions of sodium silicate (sp. gr. 1.250) at 230° Fah. with excess of hydrochloric acid. In the tank, underneath the gelatinous silica, when cleared out after 4 or 5 operations, was a layer of *extremely hard* silica, which required a very sharp steel pointed pick for its extraction. This had a fracture very like that of flint, and he had kept it till the present time without any diminution of hardness; it would not quite scratch glass, but was intensely hard. He had never published the observation.

The other point related to the concentric veins seen in the natural agate, and in those now shown. Just as albumen when coagulating in a fluid attracted to itself minute suspended particles (hence its use in clarifying sugar solutions), so colloid silica at the moment of its liberation in the nascent state, as it were, attracted to itself minute suspended particles, and it was in this way, he conceived, that these concentric veins or markings were formed from the mechanical impurities present in the solution





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