ON THE CONSTITUENTS AND GENESIS OF A FEW MINERALS PRODUCED FROM HOT SPRINGS AND THEIR VICINITIES IN JAPAN. III. CALCIUM CARBONATE MINERALS DEPOSITED FROM EFFERVESCENT SPRINGS.

By Ichizo SUGANUMA.

Received February 4, 1928. Published April 28, 1928.

Calcium carbonate when deposited from effervescent springs in Japan, rarely forms a transparent colourless mineral, and in most cases an opaque light-yellow crystalline mass. The latter is frequently contaminated with oxide of iron, sometimes mixed with oxide of manganese, silicic acid, arsenious sulphide etc. Therefore, in almost all cases, the mineral when treated with hydrochloric acid, is reduced to a small insoluble portion, while the larger proportion is dissolved with effervescence.

The mineral presents various forms and appearances, namely, a massive rock, an earthy mass, a small spherical globule, a long fibrous or sometimes white silky crystalline mass, an oolitic group etc. Which of these forms belong to aragonite or calcite, can hardly be distinguished by ordinary optical tests, though the former crystallises in a rhombic system, and the latter in a hexagonal system. At present X-ray analysis is used for the determination of crystalline system, but the apparatus employed being very complex, we often prefer a simpler but pretty accurate method. As is well known, aragonite is greater than calcite in its specific gravity, but it is difficult to estimate its value, for the mineral is of porous structure. Therefore, the author considers that the method discovered by Meigen(1) is most simple and reliable, and he has applied this method to several $CaCO_3$ minerals for the classification of them.

On the author's experiments, calcium carbonate precipitated at a temperature higher than 50°C. forms aragonite, but at a temperature lower than 50°C. it usually forms calcite. Meigen assumes that the necessary cause of the formation of aragonite is decidedly a high temperature, but his assumption is not always correct. If $CaCO_3$ is deposited in an alkaline system, the precipitate becomes aragonite even at a low temperature, while in presence of free carbonic acid or in an acidic system, calcite is always deposited.

---

(1) W. Meigen, *Centralb. f. Min.*, 1901, 577.

This latter fact was first proposed by Warth,(1) and has been confirmed by the author. For instance, if an insufficient quantity of $CaCl_2$ is added to Na_2CO_3 aq. to precipitate $CaCO_3$ in alkaline system at an ordinary temperature, we obtain aragonitic substance, while on the other hand if a sufficient quantity of $CaCl_2$ is added to $NaHCO_3$ aq. with the constant evolution of CO_2, we obtain calcite, when tested by Meigen's reactions.

Both of these precipitates consist of small crystals with an appearance of rhombohedron, although they are different in Meigen's reactions. One of them which is aragonitic in the reaction, is changed into calcite on the lapse of a few days, or sometimes even a few hours. In this case, Meigen denies the above proposal of Warth, and insists that such a substance with an aragonitic property is not really aragonite, but it is another substance such as *vaterite* for instance.

In fact, this unstable product gives the same reaction as aragonite, but is easily changeable to calcite.

On testing $CaCO_3$ secreted from the several kinds of Mollusca and lime algae by Meigen's method, the author found that most of these products consist of aragonite and ascertained their crystalline structure under microscope. The author has also collected the shells of Mollusca which have been allowed to stand 40 or 50 years, and has proved that they have been preserved as aragonite.

By these facts, it is clear that a high temperature is not necessary to obtain aragonite, in contradiction to Meigen's hypothesis.

The presence of slimy or gelatinous substance in the shells of Mollusca is also a noticeable fact, and the author comes to consider that this cementing substance is highly related to the formation of aragonite.

On the author's experiments, 1%–2% solution of gelatin is mixed with unstable aragonitic precipitate freshly prepared in a cold alkaline system, and is allowed to stand for a few months, in order to examine wheather the transformation of the above named precipitate into calcite is usual or not. After one, two or more months, the precipitate reacts aragonitic, i. e. its reaction is constant. The material treated as above is almost the same in appearance as the substance first taken, but is different in its stability, because the substance is no more unstable but exactly the same as ordinary aragonite.

Thus it is possible to obtain ordinary aragonite by precipitation at a low temperature in presence of gelatin. Generally, a gelatin solution is known as a protective colloid, and it seems to favour the formation of real aragonite.

---

(1) H. Warth, *Centralb. f. Min.*, 1902, 492.

Calcite is more stable than aragonite; therefore, the former is never changed into aragonite in the solution of gelatine. The author determined the value of P_H of both the solutions which had been prepared by boiling native aragonite and native calcite with distilled water. The result is as follows :—

Mineral.	P_H by electric method.	P_H by indicator method
Aragonite	8.2	8.4
Calcite	7.6	8.0

This shows also that there predominates the unstability or solubility of aragonite, because its hydrolysis depends upon the greater solubility.

Further the reactions of Meigen exactly coincide to the above results, i. e. on boiling the powder of aragonite with a dilute solution of $Co(NO_3)_2$, the powder is coloured violet, a basic cobalt carbonate being formed, while calcite is coloured sky-blue on long boiling with the same reagent, probably anhydrous cobalt carbonate being formed.

Furthermore, the aragonite powder suspended in water is coloured green by the addition of green vitriol, a basic ferrous sulphate being formed, while calcite on the same treatment is coloured yellow, at first probably the acidic solution of $FeSO_4$ being neutralized, and then ferric oxy-sulphate being formed by the oxydizing action of atmospheric oxygen.

It is probable that when carbonates are mixed with the solution of magnesium salts, magnesium carbonate is more or less produced, and the latter, which hydrolyses on dissolving in water, presents a noticeable alkaline reaction in the solution.

For the above reason, an effervescent spring and also sea water containing some magnesium salts have slight alkaline reactions, and have naturally a tendency of forming aragonite when $CaCO_3$ is precipitated in them.

Lastly, aragonite produced in hot springs frequently has a granular or oolitic form. Probably this is caused by the following functions :—

(1) The nucleus of the granule is deposited first with the evolution of CO_2 gas.

(2) Edges or tops of crystals are mostly dissolved by carbonic acid or are ground by mechanical revolution in water current.

Thus the precipitate becomes spherical and grows gradually through the decomposition of $Ca(HCO_3)_2$ as shown by the following equation :—

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$

This conclusion is reached by the zonal structure of spherical grobules as well as by the etch figures on their surfaces with the consideration that they are formed by a dissolving action of carbonic acid.

The First Higher School,
Tokyo.