

APPENDIX V

LABORATORY FORMATION OF MINERALS

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Geologically, the formation of crystalline minerals involves chemical reaction and precipitation. It has been recognized that many of the basic principles of physical chemistry concerned with concentration, acidity, presence of impurities, catalyzers, temperature, pressure, etc., govern not only the speed but also the form of crystallization, although the relative effects of these various factors have not been studied in detail.

In order to ascertain the possibility of forming crystalline minerals similar to those found in nature, a series of experiments have been carried on for the purpose of determining under what conditions certain of the carbonate and sulfide crystals are formed. Up to the present time, normal temperatures and pressures have been utilized in this investigation which has been conducted in the laboratory of the Missouri Geological Survey. Mr. O. C. Garst and Mr. R. A. Parker assisted in the laboratory.

In order to obtain slow precipitations, the reacting solutions were allowed to diffuse through silica gel, a method used successfully by H. N. Holmes.¹

In forming the gel, ten c. c. of a solution of sodium silicate (water glass) of 1.06 density were poured into a U tube containing an equal volume of an acid. After jelling has taken place, the desired solutions were placed in each limb of the tube. Precipitation occurs in the gel on the intermingling of solutions by diffusion.

The following illustrations indicate that perfect crystallizations can be obtained by this method. The material shown in Plate I consists of crystals and oolites, washed free of the enclosing silica gel, except in the case of galena which was photographed in the original tube. Rhythmic precipitation (Leise-gang's rings) results in many instances.

Perfect calcite crystals (Pl. I, A) were obtained by the diffusion of sodium acid carbonate (molal strength) and a cal-

¹Alexander, J., *Colloid Chemistry*, 1, 796-807, (1926), Chemical Catalogue Co.

cium salt, through silica gel. The same results were obtained where sodium carbonate was used but more complex crystals were formed. With 1/10 the molal strength thin, twinning lamellae formed but with the introduction of a small amount of manganous chloride, some cruciform-like twins were noted. The crystals shown are one months growth.

When a mixture of calcium and magnesium salts were placed in one limb of the tube and sodium bicarbonate in the other, large oolites (Pl. I, B) were formed at the zone of contact and many twin or dumbbell shaped oolites (Pl. I, C) were formed on the calcium-magnesium side of the tube along with a few small oolites. Comparatively few of the large oolites were formed with sodium carbonate or a carbonate-bicarbonate equi-mixture. An analysis after a months diffusion of half-molal solutions of calcium chloride and magnesium chloride and molal sodium carbonate showed the oolites to be nearly pure calcite along with 1% magnesium carbonate, while the dumbbell oolites contained 8% magnesium carbonate. Very small quantities of sodium carbonate and silica were also present. Some of the latter which had been growing a year had a higher magnesium content. As the analysis was performed on a large number of oolites, some of the individual particles may have had a higher magnesium content.

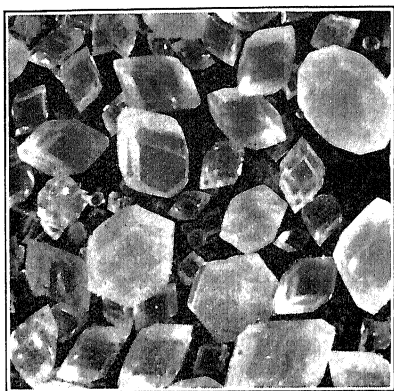
The further addition of 0.1% tannic acid represses the growth. Manganese, an impurity in natural dolomite, facilitates clustering, and when present in appreciable amounts, it is precipitated as the carbonate. The addition of a copper salt results in the formation of some brush-like particles due to radial crystallization of calcium carbonate around oolites.

The rate of formation is reduced greatly on the addition of magnesium ion to a calcium salt solution; (.02 gram instead of .1 gram is formed per month when the Mg content is raised up to the Ca content in the case of molal reacting solutions of the chlorides with a soluble carbonate).

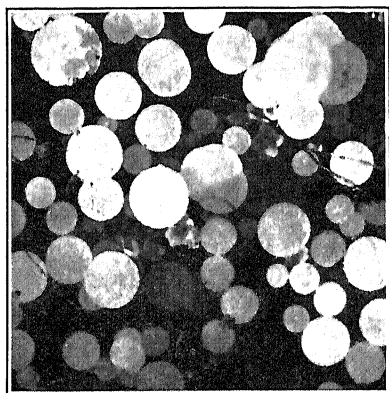
Cerussite with its typical twinning is formed by the interaction of lead nitrate and sodium carbonate (Pl. I, D). Siderite, and cadmium carbonate are similarly formed.

The interaction of copper chloride and sodium carbonate in neutral gel resulted in oolitic malachite (Pl. I, E), while with the nitrate, crystalline malachite was formed.

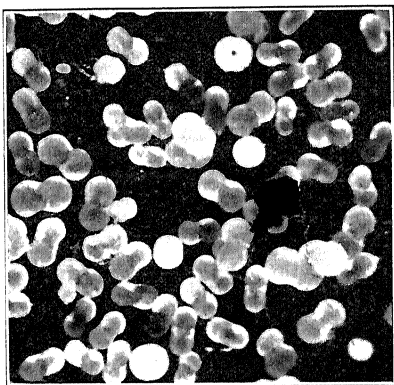
Cubic crystals of galena (Pl. I, F) were obtained on the diffusion of a water containing dissolved hydrogen sulphide,



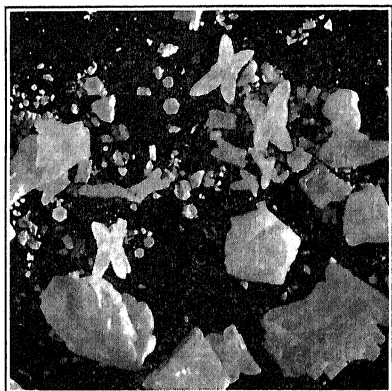
A. Calcite crystals. x 18.



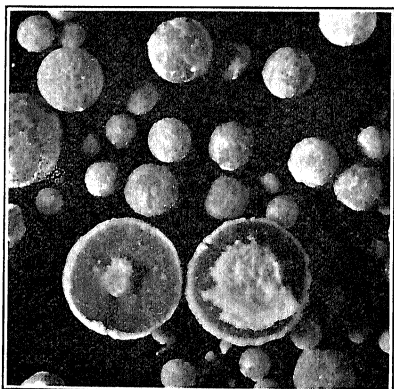
B. Calcite oolites. x 7.



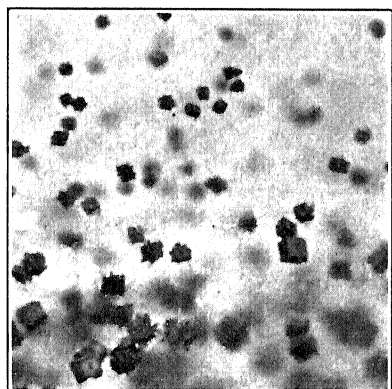
C. Twin oolites. x 14.



D. Cerussite. x 18.



E. Oolitic malachite. x 18.



F. Galena. x 18.

into a nitric acid gel containing lead nitrate. The effect of acidity on the precipitation is shown nicely in the case of sulfides—colloidal lead sulfide precipitating instead of galena crystals, except where the acidity of the gel was sufficient to repress the concentration of the sulfide ion.

In an experiment similar to the one above, colloidal cadmium sulfide was formed in weakly acid gels, but with increasing acidity, oolites of cadmium sulfide were precipitated.

That the nature of the non-precipitating anion has an effect on precipitations has long been known. Holmes¹ obtained crystalline gold in a sulfuric acid gel and colloidal gold in an acetic acid gel. The order in which acids favor crystallization seems to be, in general: nitric, sulfuric, hydrochloric and acetic. The precipitations recorded in this paper are in agreement with these data; for example, galena crystals were formed in nitric acid gel but not in the other acid gels, malachite crystals were formed with copper nitrate and oolites with copper chloride as diffusing solution.

The experimental results presented in this paper indicate that with further work additional information may be obtained relating to mineral bearing solutions. This investigation presents many possibilities in interpreting the complex chemistry of mineral deposits.

¹J. Phys. Chem., 21, 709 (1917).