

APPLICATIONS OF COLLOID CHEMISTRY TO
MINERALOGY*

PART I. PRELIMINARY REPORT

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INTRODUCTION

This report deals with a study of the growth of crystals in colloidal media, their crystal forms, and the variations in these forms obtained under varying conditions. The crystals were prepared by Dr. F. L. Simons, of the Chemistry Department of Brown University.

The study of laboratory-grown crystals of substances of mineralogical interest has many obvious possibilities. The control, however, of any such laboratory preparations has always been difficult and uncertain in most cases. We have never been able to supply those conditions of pressure, temperature, acidity, rate of diffusion, etc., that prevail during the formation of crystals in nature.

The recent developments of colloid chemistry now offer us, in part at least, a new line of attack. Gels (of silicic acid, agar, gelatine, etc.) form excellent media for the growth of crystals of almost any substance under absolutely controllable conditions that approach perhaps more closely those of nature, except for temperature and pressure, than any other laboratory method.

The results may very well be far-reaching. Earlier investigators have shown that gold or copper crystals may be prepared by reduction of the metal salts in silica gel. The connection between these experiments and the existence of gold-quartz veins is too striking to need further comment. Banding phenomena (rhythmic deposition of crystals or precipitates) which occur so frequently in gels, are undoubtedly the laboratory's answer to similar phenomena in nature.

Gels are not absolutely necessary to give us control of experimental conditions; any medium which will retard the mixing of the reagents which form the crystal will serve. H. N. Holmes has demonstrated that fine clay, powdered sulphur and even sawdust will serve. The chemist has already begun work in this field and the mineralogist should further its development.

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There are no systematic data on the influence of inert substances, acidity and the concentration on the formation of crystals by slow diffusion as in gels. Presence of inert substances or acidity, etc., may give us the explanation of the different forms of polymorphous types. The authors have, therefore, elected to take this field as a starting point and for preliminary work three simple substances—lead iodide, mercuric iodide, and calcium carbonate—were studied as these were easy to prepare and there is available data on the first two. Silicic acid formed by the interaction of acetic acid and sodium silicate was used as the gel. The lead iodide was prepared by the interaction of lead acetate and sodium or potassium iodide, the mercuric iodide by interaction of potassium iodide and mercuric chloride, and the calcium carbonate by calcium acetate and sodium carbonate. One of the reagents was incorporated into the gel before setting and the second, in aqueous solution, floated on the hardened gel. Before going intensively into this subject it was felt desirable to gain some general knowledge of the difficulties involved and to develop a technique. This paper reports some of the preliminary work.

PROCEDURE

A definite order of procedure was followed in making each specimen. 10 cc. of the sodium silicate solution were placed in a test tube first; the amount of acetic acid to be used, which varied with each experiment, was then placed in another tube. The reagent which was to be present in the finished gel was then added to the latter tube and thoroughly mixed with the acetic acid. The sodium silicate was then poured into the acetic acid and after mixing was set aside to gelatinize. After the gel had become firm (a matter of from one to six hours) the second reagent was floated on the surface, the amount usually being 10 cc.

RATE OF GROWTH OF CRYSTALS

The rate of growth of the crystals varies directly with the concentration, acidity having little effect in the experiments tried thus far. This concentration effect was to be expected as the rate of diffusion of the two reagents is a function of the concentration. The crystals began to grow immediately after the gel had set, continuing until one of the reagents was exhausted. In general the crystal growth progresses down a six inch test tube at the rate of $\frac{1}{4}$ to $\frac{1}{2}$ inch a day. Studies of the rate of growth are to be eventually included in the present research.

MERCURIC IODIDE

But two tubes of the mercuric iodide series were studied.

Tube A. 1 gm. KI in gel; saturated HgCl_2 floated on top.

Tube B. 0.15 gm. KI in gel; saturated HgCl_2 floated on top.

10 cc. of 1.062 sodium silicate; 10 cc. N. acetic acid.

In tube A six very distinct bands of red mercuric iodide were noted, the forms being ditetragonal pyramids and prisms. After the development of the last band, long, slender, prismatic crystals some 3 cm. in length were developed in the gel.

In tube B 24 distinct bands were noted, each succeeding band becoming smaller. The first six of these showed the same crystal forms as noted in A, but following the development of the last band no large crystals were formed.

In both these tubes a yellow iodide formed first. This was unstable and changed usually within 12 hours to the more stable red form. The transition temperature of these forms in aqueous solution is 127°C . Because of the rather slow transition in the gel it was possible to study these forms which are orthorhombic.

Holmes states in his *Laboratory Manual of Colloid Chemistry* (pp. 95-96) "The presence of glucose made the bands sharper. Sodium chloride diminishes the tendency to band and in sufficient concentration prevents banding altogether. If $\text{Hg}(\text{NO}_3)_2$ is floated on the gel instead of HgCl_2 still finer banding will result due to the fact that sodium chloride will not be present."

The unstable yellow mercuric iodide is not noted by Holmes in his discussion of the substance, and apparently we have found here a highly convenient method of preparing unstable crystal modifications of mercuric iodide and other substances. This observation opens a new field of possibilities.

LEAD IODIDE

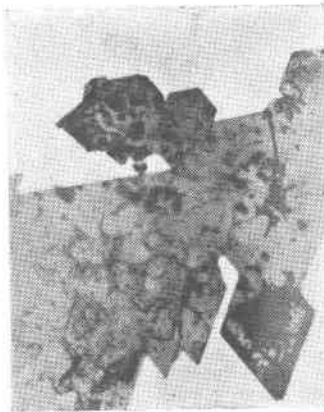
Due to the large number of different types of crystals formed of lead iodide, interesting information regarding the effects of the acidity and concentration on the development of crystal forms was obtained. Lead iodide has been prepared by this method by a number of investigators but no systematic study of varying crystal forms has apparently been made.

Series A. N/1 lead acetate in gel; 50pc. KI floated on top. In this series the acidity was varied starting with 10 cc. of acid to 10 cc. of sodium silicate and dropping off 0.2 cc. of acetic acid for each tube.

Branching forms of lead iodide (Figure 1) develop predominantly with a fair showing of hexagonal plates. These branching forms show terminations of 60° and 120° and appear to be trigonal forms grouped with the c axes parallel. They are optically negative and have an index of refraction higher than Canada balsam. (Figure 2.) Some of the fibers are simple while others are quite complex and show divergent branches. In some of the tubes hexagonal plates were attached to the fibers. These plates for the most part showed a perfectly hexagonal central nucleus.



Fig. 1

Fig. 2
×30

By varying the acidity (dropping from 10 cc. of acetic acid to 9.4 cc. of acid) the branching forms become less numerous and in the tube containing the latter acidity the best developed and the most numerous hexagonal plates are developed. As the acidity was further decreased the plates began to disappear. It appears, therefore, that the above acidity is the transition point between these two forms. When the acidity was dropped to 8.0 cc. there was a pronounced diminution of the platy forms.

Series B. This series carried the decrease in acetic acid still further and when 7.6 cc. of acid were used the plates disappeared altogether. Sodium iodide was used instead of potassium iodide.

Series B₁. This series parallels B with the concentration of the lead acetate in the gel cut to 50 pc. There is a noticeable dropping off of platy forms and when 6.8 cc. to 6.4 cc. of acetic acid were

used no plates developed. Rough hexagonal outlines are noted and the slide shows platy developments with a hexagonal nucleus about which are grouped roughly outlined hexagonal forms (Figure 3).

Series C. 1 cc. of 3N. solution of sodium iodide was incorporated in the gels of varying acidity and saturated lead acetate floated on top. The branching forms diminish considerably and when 7.0 cc. of acid were used there appeared no branching forms. This was the only tube in which none of these forms were present. The hexagonal plates reach their strongest development in this tube.

The procedure followed in series A, B and B₁ was to float KI on the gel. In series C where the iodide was placed in the gel matters were complicated by the presence of a double salt of varying composition ($\text{PbI}_2\text{-Pb}(\text{Ac})_2$) along with the fibrous and platy forms discussed. These double salt crystals also appeared in A, B and B₁ but in relatively small numbers. While the double salt was purely incidental and not the main object of the study, the variations in its crystal forms were sufficiently interesting to warrant mention in this paper.

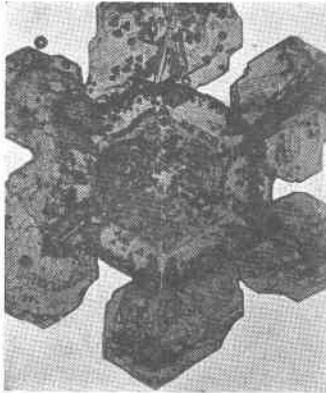


Fig. 3
×45

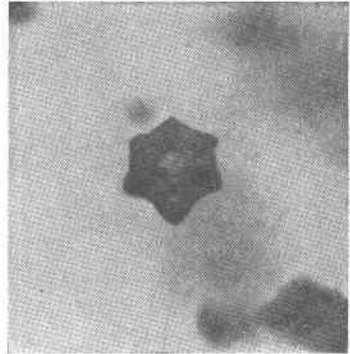


Fig. 4
×60

The first form of this double salt to appear was a snowflake crystal. These forms are pale yellow in color as contrasted with the orange color of the plates and fibers. When the acidity of the gel is kept the same and the concentration of the sodium iodide reduced 50 pc. numerous orthorhombic forms appear. Cruciform twins are quite abundant. As the alkaline end of each series

is reached the double salt becomes more prominent and simple crystals are more numerous than cruciform twins.

The double salts formed due to the fact that the concentration of the reagent in the gel greatly exceeded the concentration of the reagent diffusing downward from above. The end members of series B and B₁ which differ in their concentration show radically different forms. The former were commonly combinations of domes and prisms of the orthorhombic system with a few pyramidal terminations. Some apparently hemimorphic forms were also noted. The end members of series B₁ showed peculiar prismatic stalk-like crystals with fibrous forms grouped about one or both ends. In some cases there was a radial grouping present. These forms resembled very strongly the stalk and petals of a flower. ✓

The presence of inert salts, although not radically affecting the forms of the double salts, did produce some new types. In the presence of NH₄NO₃ which was incorporated in a gel of type of series A, domatic forms became less prominent and spherical groupings were noted. When the amount of ammonium nitrate was trebled but one cruciform twin was noted. KNO₃ added to a similar gel in small amounts seemed to have no effect upon the forms.

CALCIUM CARBONATE

The crystals were prepared by the usual general method using 0.5 cc. to 1.00 cc. N/1 calcium acetate in the gel and N/1 sodium carbonate floated on top. Experimental data on these forms are at present meagre. All specimens showed a multitude of very small rhombohedrons of calcium carbonate fairly well developed. In most of the tubes the rhombohedral forms of calcite were present with forms resembling pseudo-hexagonal twins of aragonite (Figure 4). Varying the acidity between rather wide limits seemed to have no effect on either the abundance or the type of crystals produced. Studies of the effect of varying concentrations have yet to be made. The presence of forms resembling aragonite in this series is a very important point for obvious reasons.

SUMMARY

1. This paper calls attention to the value of studies of laboratory grown crystals of substances of mineralogical interest providing

such laboratory conditions can be adequately controlled and can approach in some measure those found in nature.

2. The use of colloidal media such as silica gel is suggested as a method of obtaining such control.

3. The authors have undertaken a detailed study of the effect of acidity, presence of inert substances, concentration and diffusion phenomena on the formation of crystals.

4. Preliminary experiments with lead iodide, mercuric iodide and calcium carbonate, carried out to obtain a general idea of the difficulties involved and to develop an experimental technique, indicate the following: (a) Rate of crystal growth in the cases studied is not affected by the acidity of the medium. (b) Unstable polymorphous forms may be held in 'suspended transformation' long enough for convenient study. (c) Concentration and acidity have a very decided influence on crystal form. In some cases the two factors are interdependent. (d) Studies of calcium carbonate indicate that the conditions determining which crystal form a substance may take (i.e. calcite or aragonite) are within experimental reach.

BARYSILITE FROM FRANKLIN FURNACE, NEW JERSEY

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Barysilite, a lead silicate hitherto known only from Långban and Pajsberg, has recently been identified at Franklin Furnace. It was found on the picking table in a few small masses and its chemical character was first recognized by members of the staff of the chemical laboratory of the New Jersey Zinc Company. Material was sent by them to the Harvard Mineralogical Laboratory, together with a preliminary analysis. It was at first thought to be alamosite but its true nature appeared when the analysis given below had been made on purer material.

The barysilite occurs, in the single specimen examined, as a massive, pink to colorless mineral, associated with yellow garnet and colorless willemite. There are, however, occasional druses of minute pink crystals of the mineral, too small for crystallographic