APPLICATIONS OF COLLOID CHEMISTRY TO MINERALOGY
PART II. STUDIES OF CRYSTAL GROWTH IN SILICA GEL

L. W. Fisher and F. L. Simons, *Brown University*

In a preliminary report[1] the authors discussed the value of silica gel as a medium for the growth of crystals, and presented the results obtained in preliminary trials with lead and mercuric iodides and calcium carbonate. In the present paper the results are given of further studies of lead iodide.

Although the method of procedure was described in the previous paper a brief review of this point seems desirable. The silica gel used was formed by a mixture of aqueous Na_2SiO_3 (1.062 sp.gr.) with varying amounts of N/1 CH_3COOH. Equal volumes of silicate and acid give a gel of decidedly acid reaction; neutrality is approached only when approximately two volumes of silicate are used to one of acid. The crystals were prepared by chemical reaction of two reagents (e.g. lead acetate and sodium iodide for the lead iodide) one of which was incorporated in the gel before the latter had set, the other being poured over the top of the hardened gel. The latter reagent diffusing downward causes slow formation of crystalline material. Ordinary six inch test tubes were used as containers.

A rather complete study of the lead iodide crystals formed in gels under varying conditions of acidity, concentrations, etc., has been completed and some interesting data obtained. Five separate series each consisting of eleven tubes were prepared in

Series A. 10 cc. of sodium silicate.
10 to 6 cc. of N/1 acetic acid to form gel.
1 cc. N/1 $Pb(Ac)_2$ in gel.
10 cc. N/1 NaI "floated" on gel.
Series B. Same as A but KI substituted for NaI.
Series C. Same as A. but concentration of Pb $(Ac)_2$ halved.
Series D. Same as A but $Pb(NO_3)_2$ used in gel in place of $Pb(Ac)_2$.
Series E. 10 cc. of sodium silicate in gel.
1 cc. 3N. NaI in gel.
10 cc. saturated $Pb(Ac)_2$ "floated" on gel.

Note: Acetic acid varied in each series from 10cc. to 6 cc. by steps of 0.4 cc.

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[1] L. W. Fisher and F. L. Simons; Applications of Colloid Chemistry to Mineralogy. Part I. Preliminary Report. *Am. Mineral.*, **11**, 124—130 (1926).

order to study the effects of both acidity and concentration on the crystals formed.

RATE OF GROWTH

Fibrous forms of lead iodide discussed in the preliminary report are predominant in the more acid members of the series—A, B and C. The rate of growth of the fibers is rather uniform and is not visibly affected by the degree of acidity in any individual series. In every tube the average growth in one day is one centimeter, this rate decreasing until one of the reagents is exhausted. In this study and in the preliminary work it seems then that acidity has no effect on the rate of growth of the crystals.

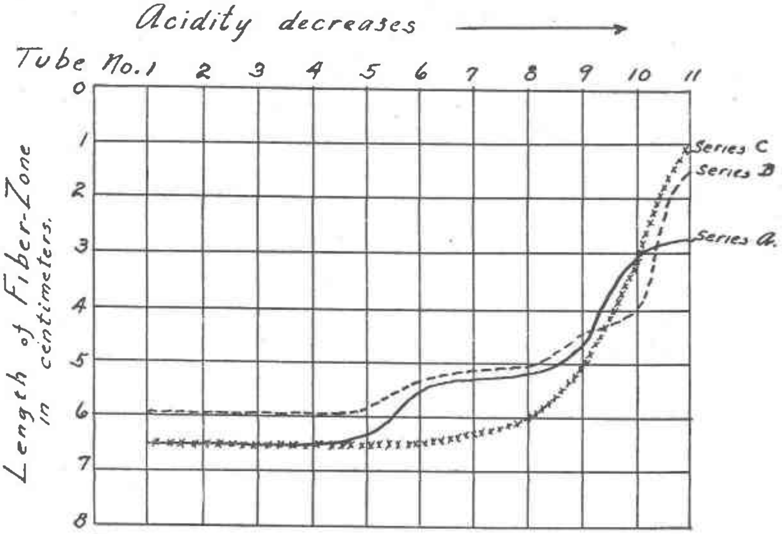

Fig. 1. Curve showing rate of growth of the fibrous zone.

In the more acid members of each of the three series under discussion the fibers grew to a depth of 6.5 cm., the longest individual fiber reaching an overall length of 6 cm. The depth of growth, that is, the length of the fibrous zone, decreases as the acidity decreases. Interesting data on the length of the fibrous zone were obtained by varying the floating reagent and decreasing the concentration of the reagent in the gel. In series A, as shown in the accompanying graph, figure 1, the fibrous growth shortens abruptly between the 9th and 10th members of the series, whereas the decrease was more abrupt in B when KI was used between the

10th and 11th members. In C the concentration of lead acetate was cut down in the gel and the fibrous zone decreases gradually beyond the 8th member. These data indicate that the concentration of the solution within the gel and the type of reagent floated exert an influence on the rate of growth of the crystals.

The hexagonal crystals which formed in plates and accompanied the fibrous growths show these same effects. Plates are abundant in A until the middle of the series is approached and then there is an abrupt decrease. This decrease is more pronounced near the end of series B. Thus it would be indicated that with KI used as a floating reagent the plates are more persistent in the neutral end of the series than they are when NaI was floated on the gel. When $Pb(NO_3)_2$ was incorporated in the gel in place of lead acetate the plates persist farther through the series and are seen in all tubes although they are in the minority in the latter half of the series.

Fig. 2

Fig. 3

Fig. 4

A Discussion of the Forms

Series A: The first nine members of the series are predominantly fibrous in their forms. The more acid members of the series show strong development of hexagonal plates to tube 7 when they drop off rather abruptly, and bundle, twin or simple crystal forms of double salts ($Pb(Ac)_2$, PbI_2) are formed.

The fibrous forms are typically fern-like and show a growth of from 2 to 2.3 cm. during the first day and then grow at the rate of about a centimeter a day. They tend toward spearheaded terminations throughout. In the acid end of the series some small trigonal plates are noted but these are decidedly in the minority. All through this series there seems to be a tendency toward the formation of trigonal forms although they never become abundant. The plates in this series are not usually radially or zonally marked.

Fig. 2 (left center) shows the characteristic spearhead fiber along with some simple hexagonal plates, not marked radially, and one large trigonal form.

The double salt first develops in the middle member of the series and from this point to the end of the series its forms perdominate over the simple hexagonal and fibrous forms of simple lead iodide.

Series B: No pronounced difference exists in the development of forms in this and the preceding series. One or two exceptions to this might be stated. The fibers in this series are for the most part less divergent than those of A, and are quite simple in their development. Trigonal forms are a bit more common but are not in the majority. The fibrous growth stops more abruptly in the neutral end of the series than it does in A.

A bundle growth of the pale yellow double salt was noted in the middle member of this series in approximately the same position as in A. Some small truncated trigonal forms were seen in the second member, and these, too, correspond to their position in series A.

Series C: The fibers again assume more divergent properties analogous to those already cited. They are quite broad in their general development grading off gradually into short, stubby fibers toward the neutral end. The gradation in this series is more gradual and progressive than in either of the preceding series. No tube in this series shows as many hexagonal plates or trigonal forms as its corresponding member in the other series. The development of the double salt is perhaps stronger in the last three members than in the preceding series. Trigonal forms are somewhat more abundant in the early members of the series than in the latter.

Series D: In this series lead nitrate was used in the gel in place of lead acetate and a radically different development of forms was noted. This may be due to one or more of several causes, e.g.—(1) the fact that $NaNO_3$ is present; (2) the different solubility of lead nitrate; and, (3) the different degree of ionization of lead nitrate.

The trigonal forms which were previously indicated by the spearhead terminations of the fibrous forms and also by scattered plates throughout the first three series now become more predominant. Scattered fibers are seen in the first members of the series but they are never as prominent in this series as noted previously. They do not attain the length of those in series A, B and C but their terminations are similar to those shown in figure 2 and are, in the main, trigonal, with some hexagonal plates attached.

The first tube of the series shows the best development of fibers and with them are associated plates usually radially or zonally marked, and some scattered trigonal plates. An excellent example of the radially marked plate is seen in figure 3 where it is associated with other plates, both plain and radial. Figure 4 shows another type of a radially marked plate along with a trigonal form grown through a hexagonal plate. As the acidity of the series is decreased the plates become more numerous until the 5th tube is reached when they attain their maximum development. The best trigonal types were noted in this tube and are shown in figures 5 and 6. The field in figure 5 shows a trigonal plate overlying a hexagonal plate and also a radially marked hexagon. In figure 6 the radially marked trigonal form which is quite abundant is shown along with a large, plain hexagonal plate.

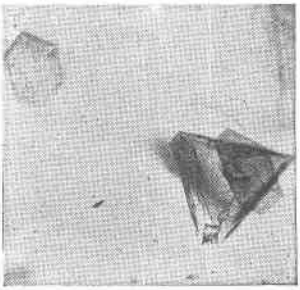

Fig. 5

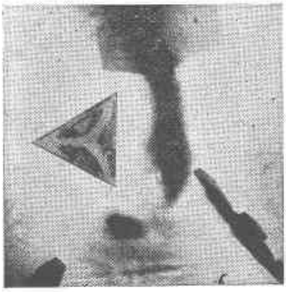

Fig. 6

In this tube transitional forms between the normal hexagonal and trigonal were noted. A number of crystals were combinations of the rhombohedron cut by a basal pinacoid and some hexagonal prisms cut by rhombohedron and basal pinacoid. These forms are, however, not in the majority. The fibers except in the acid members of the series never extend below the second days' growth. The trigonal forms decrease decidedly when the neutral end of the series is approached but maintain their development throughout the entire series.

The double salt does not appear in this series until the last two members are reached and then the forms differ from those previously studied in that they are generally monoclinic prismatic forms with scarcely no bundle types noted. In these two tubes the double salt is strongly predominant over the simple crystals of the hexagonal and trigonal types.

From a study of the interference figures of radially marked plates as shown in figure 3 it seems possible that these types are made up of six trigonal prisms and are not normal hexagonal types. Radially marked trigonal plates as shown in figure 6 show perfect basalt section figures. All the types of plates, trigonal or hexagonal, plain, radially or zonally marked are negative optically. The mean index of refraction is higher than Canada balsam.

Series E: Increasing the concentration of the NaI threefold and incorporating it in the gel and floating a saturated solution of lead acetate on the gel prevented the formation of fibers altogether. The crystallization of the double salts is more prominent and rapid and plates of hexagonal characteristics were found only in the first member of the series. They were well developed but relatively few in number.

DOUBLE SALT CRYSTALS

Bundle Types: These are made up apparently of monoclinic combinations of domes, pinacoids and prisms, and are the first forms of the double salt to appear in any series. (They are always a lemon yellow color as contrasted with the orange color of the normal lead iodide crystals). In series A and B they begin their development at approximately the same period. A6-5cm., B6-5.7cm.; A7-4.5cm., B7-4.2cm.; A8-end of second day, B8 directly below the beginning of the second day's growth; A9, first day's growth, B9, the same. (The cm. notation means the distance from the top of the gel.).

Since their development seems to be rather uniform it is seen that there is apparently no influence exerted on them by the floating reagent, for A and B differ only in this respect. In series C these forms were first noted in tube 30 which corresponds to A8 and B8.

Series E shows the forms in their strongest development and since this tube has much stronger concentration of reagents, and series C only half the concentration of A and B, the formation of the double salt is a function of the concentration of the reagents used.

Stalk-Like Forms: These forms are most abundant in the neutral end of the series except in C. They usually occur after the first indication of the double salt bundles and are not scattered throughout the tubes to any extent except when the extreme neutral end is approached. Despite the strong concentration of Series E no stalk-like forms are noted anywhere in the series.

Radial Growths: A peculiar form maintained by the double salt is first seen in small amounts in the first three series and becomes quite pronounced in series E. There is a rather strong development of simple crystals of the double salt-monoclinic prisms, pinacoids and domes, and as the acidity of the series is decreased the forms unite to produce rather thick bundles of crystals which are not the same as noted under bundle types. Later developments of cruciform and fish-tail twins are noted and in the last member of the series, thick, nodular types spread more and show radial growths of monoclinic crystals from a common center.

The crystal forms described under double salts are of doubtful value as the composition of the double salt probably varies, viz., (1)$Pb(Ac)_2.PbI_2$; (2)$Pb(Ac)_2.2PbI_2$; (3)$Pb(Ac)_2.3PbI_2$; etc., These three compounds are known and there must be more. We are unable to state at the present time which of the double salts we are dealing with.

THE SIGNIFICANCE OF STRAIN STRUCTURE IN QUARTZ FROM DUCKTOWN, TENNESSEE

Paul F. Kerr *Columbia University*

The so-called quartz "floors" in the copper mines at Ducktown, Tennessee, have furnished specimens of transparent quartz of rock crystal quality. Aside from the clearness of the mineral, in itself unusual, it attracts attention on account of a peculiar crossed ribbon structure which it exhibits. One specimen recently examined[1] shows a surface measuring three by five centimeters in area, approximately flat and neatly engraved as if by machine work with two intersecting sets of curved ridges cutting each other at acute angles. The appearance of the area may be compared to the "engine turning" on the back of a watch, a term

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[1] A specimen kindly supplied by Professor J. F. Kemp.