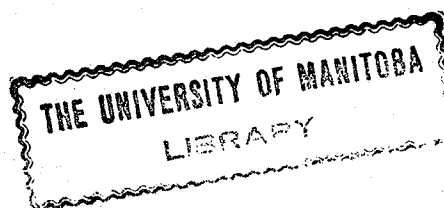The Function of Gels in the Formation of

Pegmatites, and of Quartz and Carbonate Veins.

by

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# Contents

# I.  Introduction.

The application of the principles of colloid chemistry to Geological problems is of very recent growth.  Van Bemmelen in 1899 outlined many of its fundemental problems;  it was not however until 1909 when Cornu published his classical papers on colloidal mineralogy that it attracted much attention.  Since then numerous other papers have appeared and the literature of the subject has already become extensive.  So far geologists have chiefly confined their attention to the part colloids have played in sedimentary processes, and the smaller though still very important branch, the function of colloids in primary ore deposits, has been almost totally neglected.  The question of gels in primary veins has especially been overlooked.  The deeply eroded and now exposed veins of the moderate and deep seated zones do not today contain gels, whereas the shallow veins occassionally do, and it has been assumed that the higher temperatures of the former would have prevented the formation of gels.  But the relationship of pressure to the retention of water by a gel has not been considered and it is the purpose of this paper to show that gels can and do exist in all types of primary ore deposits, from the high temperature pegmatite to the shallow, low temperature vein.

Silicic acid gel is here considered to have played a very important rôle in the origin of pegmatites and quartz veins;  also under certain conditions carbonate gels were formed and locally have been of consequence.  The probable existance of other gels in veins is indicated and the chemistry of gels is summarized in order to show the similarities between gel precipitation and ordinary precipitation to which latter process vein formation is generally ascribed.

By the crystallization of minerals from these gels many of the structures common in ore deposits such as the large crystals of pegmatites

the concentric rings and banding of minerals, and the dendritic and arborescent crystals, are explained. Furthermore the presence of angular unconnected inclusions in veins is explicable on the assumption that they were buoyed up by a viscous gel mass.

## II. Gels

I. The Definition of Gel, Jelly and Gelatinous Precipitate.

The words gel, jelly and gelatinous precipitate, have carelessly often been used interchangeably, but the general custom and the one here adopted is that of using gel as the inclusive term embracing both jelly and gelatinous precipitate. A gelatinous precipitate is a gel which shows syneresis, that is when first formed it sets to a stiff viscous mass and then immediately contracts squeezing out part of the liquid. A jelly does not show syneresis.

Gels have often been considered as coagulated emulsions but the distinction between emulsions and suspensions has lately been broken down, as many substances have been prepared in both the suspensoid and emulsoid state. An emulsion is generally defined as a liquid dispersed in a liquid medium and a suspensoid as a solid dispersed in a liquid medium; but are the colloidal particles of a suspensoid realy solid? Can a solid retain its crystalline properties on extreme subdivision? May not the greatly increased surface tension, dneto the enormous sur- face developed, deform the minute crystals and tend to form spheres? It has been observed microscopically that on crystallizing, small spherical bodies and globulites first form. (Ref. 1) Even, however, if we assume that an emulsion is a liquid dispersed in a liquid, the conception that a gel is a coagulated emulsion is no longer tenable, for Von Veimarn has shown that gels are simply solvated precipitates formed from solutions above a certain degree of supersaturation, and

that theoretically any substance can be obtained in the gel form.
It is not necessary to assume that these gel precipitates are de-
finite solvated compounds. In fact a series of experiments have
conclusively shown that they are not. Davies (Ref. 2) by pro-
longed heating of hydrous ferric oxide under water completely
dehydrated it, proving that no hydrates were formed. Ramsay (Ref.
3) found that the rate at which hydrous ferric oxide lost water
was not constant and consequently there could not be any definite
hydrate within the temperature range studied. Van Bemmelen (Ref.
4) determined the isotherm for ferric oxide and water and found
no indication of a compound, as was also the case for the vapor
pressure curves obtained for silicic acid jelly. (Ref. 5) It
is assumed that the liquid of a gel is powerfully adsorbed and
thus retained (Ref. 6).

2. The Production of Gels and Von Veimarn's Law of Corresponding
   States for the Crystallization Process.

Von Veimarn (Ref. 7) has developed and substantiated by a great
variety of experiments a law which he calls, " The Law of Corres-
ponding States for the Crystallization Process," which may be
stated thus: The degree of dispersion and the general physical
appearance of crystalline precipitates are always the same irres-
pective of the chemical nature of these precipitates, provided
that the precipitation takes place under corresponding conditions.

If we take the case of the double reaction  AB plus MN gives
AM plus BN, where AM is a precipitate, then the law may be stated
mathematically thus:

$$D = \frac{Np}{Sp} . V.K(AB).K(MN).K(AM).K(BN)$$

where D is the dispersion coefficient of the precipitate (AM) and

describes the degree of dispersion and the general appearance of the precipitate.

Sp is the solubility in equivelents per liter of the precipitated substance AM.

Np is the number of equivelents of the precipitate AM which must be deposited out of each liter of the solution in order that its concentration shall be reduced to Sp equivelents per liter. In other words it is the amount of the precipitate in excess of the amount soluble.

V is the viscosity of the solution.

K(AB), K(MN),K(AM),K(BN) are coefficients expressing the degree of complexity (chemical, physical or both) of the various substances in solution.

In the case of substances having a comparitively simple chemical structure and which are not associated in solution, the above equation becomes $D = \frac{Np}{Sp} \cdot V$ and the most important factor here is $\frac{Np}{Sp}$ which is called the degree of supersaturation of the solution.

Using this law Von Veimarn has prepared precipitates of such materials as sodium chloride, barium sulphate, aluminium hydroxide, silver chloride and many others in almost any desired degree of dispersion, the precipitates ranging from coarse crystals to jellies.

The application of this law to the formation of gels can probably best be shown by considering a definite reaction and the resulting types of precipitates formed from different degrees of supersaturation.

Let us take the reaction $Ba(CNS)_2$ plus $MnSO_4$ gives $BaSO_4$

plus $Mn(CNS)_2$ in which equivelent quantities of $Ba(CNS)_2$ and $MnSO_4$ are used.

If we mix $\dfrac{N}{20,000}$ solutions then the resulting quantity of $BaSO_4$

will be $\dfrac{1}{20,000}$ of one equivelent and since the solubility of

$BaSO_4$ is about $10^{-6}$ equivelents per liter, then the value $\dfrac{Np}{Sp}$

would be 0 to 3 for concentrations $\dfrac{N}{20,000}$ to $\dfrac{N}{7,000}$. In this range

a few large crystals will form, crystallization starting around
dust particles or places where the vessel has been scratched. In
the case of $\dfrac{Np}{Sp}$ less than 1 it takes several years for the crys-
to form.

Between values $\dfrac{Np}{Sp}$ from 3 to 48 a fine powder containg micro-

scopic crystals forms. At value $\dfrac{Np}{Sp}$ equals 48, about an hour is

necessary for precipitation.

If the degree of supersaturation is less than 48 and there is
some material in the solution that the particles can adsorbed and
thus become charged, a suspensoid colloid will result.

With values $\dfrac{Np}{Sp}$ between 48 and 22,000 needle, skeleton and star

shaped crystals are produced. A suspensoid can form but is very
unstable and settles in a short time.

With values $\dfrac{Np}{Sp}$ 22,000 to 87,600 the precipitate is at first

granular, then curdy, flaky and finally gelatinous in character.
The so called amorphous precipitates are however composed of
crystals.

With values $\frac{Np}{Sp}$ greater than 87,600 gelatinous precipitates and
jellies form.

The only essential therefore to produce a gel is that the value
$\frac{Np}{Sp}$ be greater than 87,600 and when this is the case in ore form-
ing solutions, gels will result. The solubility of many ore min-
erals is almost zero and consequently reactions producing them,
even in extremely dilute solutions, would exceed this value and
give rise to a gel. For example, quartz is listed as insoluble
in water in tables of solubilities where figures as low as 0.00001
grams per liter are given. Assuming this value for the solubility
of quartz and water, $\frac{Np}{0.00001}$ must exceed 87,600 in order to produce
a gel. In other words Np must be greater than 9 parts of quartz
to 10,000 parts of water. But the actual composition of ore solu-
tions and the solubility of quartz in them is unknown, so that the
above value would not be strictly applicable to vein quartz.
Nevertheless, this value is so small that it points to the possi-
bility of silica gels in ore deposits even though the solubility
of quartz in ore solutions may be much greater than in water.
When certain features of veins indicate crystallization from a gel
the question deserves further consideration.

III. The Relation of Gels to Pegmatitic Growths.

1. Introduction.

The origin of pegmatites and their coarse crystalline character
has long been a much disputed problem in geology. Much of the
controversy has centred on the differences of composition between
the pegmatites and other igneous rocks, the relation of mineraliz-
ers to viscosity, and the effect of these various actors on the

texture of the resulting pegmatite. An excellent summary of the voluminous literature on this subject has been given by J. B. Hastings (Ref. 8).

Concerning the definition of a pegmatite, Harker (Ref. 9) writes: "The original pegmatite of Hauy (1822) was a coarse graphic intergrowth of feldspar and quartz (graphic granite) but the name was extended by Delesse (1849) to all coarse rocks, whether graphic or not, these occuring commonly as veins or dykes traversing an ordinary granite, or as apophyses, or a more or less continuous fringe on its border. Subsequent usage has further extended the term to cover corresponding modifications of other plutonic rocks, such as syenite, diorite, gabbro."

The word pegmatite is used in this paper in the above sense.

The modern theories of the origin of pegmatites all favour crystallization from a magma of low viscosity, whose fluidity is due to the presence of water and gases. The magnitude of the rôle played by the gases is uncertain; some investigators give it considerable importance, whereas others give it a subordinate role. But most agree that the presence of a relatively large amount of water has been an essential factor in the development of pegmatitic growths.

In this paper it is maintained that water and gases, when present, have affected the crystallization, but only to a minor degree, and contrary to the prevailing idea it is held that pegmatites crystallized, not from a fluid magma, but from a viscous silicic acid gel.

2. A Critical Survey of the Causes which may influence Pegmatitic Growths.

Bastin (Ref. 10) has made an admirable survey of the origin of the pegmatites of Maine.  The following points may be noted:

1.  The textural differences between granite and granite pegmatites of Maine could not have been due to differences of temperature and pressure because:

(a)  In many places pegmatites were found cutting granitess, both of which were consolidated from the same igneous intrusion.

(b)  In places pegmatites were found actually enclosed by granites.

(c)  Granites were found grading into pegmatites.

Obviously, then, pegmatites and granites were formed under the practically the same temperature and pressure.


2.  The textural differences between granite and granite pegmatites of Maine, could not have been due to differences in constituents:

(a)  The essential constituents of the pegmatites are the same as those of the granites and practically in the same proportion, though slightly more acid.

(b)  In the case of the minor constituents, although many rarer minerals occur chiefly in pegmatites, yet most pegmatites contain very few or no rare minerals.  By far the greater nimber of the pegmatites of Maine contain no unusal or rare minerals.  Thus in many cases, pegmatites have developed their peculiar texture and no rare minerals have been left to indicate that mineralizers like fluorine, chlorine, or boron, etc., were ever present.  While these elements, when present, may contribute to pegmatitic structure, they are not essential.

From the above it would seem that differences in the composition of the essential or minor constituents of pegmatites have not

caused the pegmatitic texture.

3. The textural differences between granites and granite pegmatites, of Maine, could not have been caused by the gases because:

(a) If the gases existed when the pegmatite magma cooled they must either have been occluded or escaped:

(i) The escape of such material, especially chlorides, fluorides, or borates, would cause contact metamorphism, whereas there is no evidence of contact metamorphism.

(ii) If the gases have remained and become occluded then the pegmatites should have a greater percentage of gases than the granites, but Bastin found no noticeable difference in the gas contents, nor were miarolitic cavities more common in the pegmatites.

Thus from the evidence presented by Bastin it is seen that the textures of the Maine pegmatites are not due to different conditions of temperature and pressure, not to the differences in the constituent minerals or volatile gases.

Many investigators have laid great stress on the importance of the so-called mineralizers in the formation of pegmatitic growths, their effect being attributed to lowering of the viscosity and the lowering of the melting point of the magma. But, as has been seen, this has been over-emphasized. In addition to Bastin's criticism it may be pointed out that the flourine, chlorine, boron, etc., could not possibly exist as such in pegmatites, because they would attack the silicates or even quartz. Water itself attacks silicates or quartz and forms silicic acid at the temperature of pegmatite formation. For similar reasons the acids such as hydrofluoric acid, hydrochloric acid, could not exist as

such. When present, these elements must be in chemical combination as minerals radicals, such as found in chlor-apatite, topaz, or tourmaline, and while these might favour fluidity or lowering of the melting point, they certainly would not do so to the extent as that inferred for free fluorine, chlorine, hydrochloric acid, or other mineralizers.

### 3. Theory of the Origin of Pegmatites.

In the previous section various factors which might have affected the pegmatitic growths have been discussed and found to be inadequate in themselves to account for the textures. We shall endeavour to show that the essential cause of pegmatitic growths is crystallization from a silicic acid gel, which results in the formation of large crystals.

The process by which silicic acid would be formed may be briefly presented. The original basaltic mother magma, of Daly and Bowen (Ref. 11), from which differentiation produces the granites, gabbros, and other igneous rocks, does not contain quartz. Later processes of differentiation produce the quartz, which must have come from the decomposition of the original silicates. This change of silicates to anhydrous quartz could not have taken place directly, but intermediate silicic acid must have been formed since the magma contains water. All silicates on decomposing in the presence of water forms silicic acid. Silicic acid is formed by the action of steam, carbon dioxide, alkaline carbonates, or acids if present, on the silicates. (Ref. 12) Even water and feldspar on prolonged heating produce silicic acid.

The small amount of silicic acid so formed in the solidfying magma rises to the top of the reservoir, since it is immiscible

*Pegmatite should than always be forming on top of granite.*

in and lighter than the silicates of the magma. Thus a well of
silicic acid accumulates at the top and this may later be squeezed
out into fissures forming pegmatites and veins. The difference
between pegmatitic and granitic texture are thus due to the compa-
ritive absence of silicic acid gel in the latter, since silicic
acid has separated to the top. In brief, pegmatites have crystal-
lized from a silicic acid gel, whereas other igneous rocks have
not.

Mineralizers, so called, if present have little effect on the
stability of the silicic acid gel. For instance, tungstic acid
or molybdic acid would increase the viscosity of the gel very
slightly and would protect the gel from the peptizing action of
the alkalies.

4. Proof that Gels favour the Formation of Large Crystals.

Hatschek and many other experimenters found in investigating
Leisegang rings that unusually large crystals were developed.
Hatschek obtained lead chloride crystals 15 mms. long in agar.
Holmes (Ref. 13) produced crystals of silver dichromate in silicic
acid gel which in one month grew to the size of 5X5X1 mms. Gold
and many other substances have also been crystallized from gels.
In all cases unusually large crystals have been obtained, much
larger than would have been produced without the use of the gel.
For example, if $\frac{N}{10}$ lead acetate be added to 2N potassium iodide
a lead iodide precipitate is formed which does not show crystalli-
ne outlines to the eye, but if the lead acetate is placed in a
silicic acid gel and the potassium iodide is allowed to diffuse
into it, the resulting lead iodide is noticeably crystalline.
Perfect hexagons of nearly 5 mms. dia. can be obtained by this

method. Accprding to Holmes (ref. 13) theory, the action of gels in favouring large crystals is chiefly due to the capillary structure of the gel, which retards diffusion greatly. As is well known large crystals are formed if diffusion is very slow. De Schulten, by the slow admixture of extremely dilute solutions of barium chloride and sulphuric acid, obtained crystals of barium sulphate that in a month measures 5 mms. Dreaper obtained large crystals byn using a single capillary tube filled with 3% lead acetate and immersed in 5% hydrochloric acid. Crystals of lead chloride nearly 1 mm. long formed in the capillary tube due to slow diffusion. Holmes (Ref. 14) obtained large crystals by allowing the reacting solutions, to diffuse through pwwdered silica, gelatin, agar, flowers of sulphur, barium sulphate, etc. Without doubt any compact mass of insoluble particles may function as a gel in favouring the formation of large crystals.

5. Suggestive Forms of Crystallization found in Pegmatites which can be reproduced in gels.

Radiating aggregates, tree-like, or leaf-like forms, etc., are all easily prepared by allowing substances to react in a gel. One well known example is the lead tree prepared by Simon (Ref. 15) in a silicic acid gel containing lead acetate. A piece of zinc or tin was pressed into the top of a silicic acid gel, which had set, and a splendidly branching tree of lead formed in a few days. The silicic acid gel was made by adding equal volumes of N acetic acid to 1.06 specific gravity sodium silicate, then adding lead acetate and allowing the liquid to set tó a gel.

Similarly radiating tetrahedrons of copper can be made by reducing copper sulphate in silicic acid gel by hydroxylamine hydro-

-chloride (ref. 16). Freezing of gelatin gel containing water produces aborescent ice crystals. Though it is possible for radial aggregates, tree-like forms, etc., to be formed without the use of a gel, yet they are so easily produced, and so characteristic of crystallization from gels, that the well-known radiating crystal types and occasional aborescent and dendritic types found in pegmatites suggest a crystallization from a gel origin.

We quote a few references:

Lindgren (Ref. 17), "Spodumene occurs in Etta Mine, Black Hills South Dakota, in crystals resembling tree trunks as much as 42' in length."

Williams Ref. 18), "Long crystals of black tour,aline forming radiating groups sometimes two feet in diameter."

Fairbanks (Ref. 19), "Near southern end of this vein is a deposit of lepidolite mica 10 feet thick at the widest part and apearing in detached bodies for several hundred feet. It is fine grained, shows a pale purple color. In places it is pure, in others filled with large aggregates of pink tourmaline (rubellite). Some of the aggregates are a foot across, others are long and slender with aborescent forms."

## 6. Are Pegmatite Magmas Fluid or Viscous?

According to present conceptions pegmatites are supposed to have crystallized from a fluid mass; whereas according to the gel hypothesis they crystallized from a viscous mass.

Several geologists have observed that the pegmatite magma must have been viscous.

As far back as 1885 Blake (Ref. 20) writes concerning the pegkatites of Black Hills: "All the constituents of the dike appear

to have crystallized from a semi-fluid pasty magma, in which the
elements were free to arrange themselves from one side of the dike
to the other and to crystallize out slowly.  This is indicated in
several ways, but strikingly by gigantic crystals of spodumene
stretching across the mass at Elta in straight lines for 20 to 40
feet in the midst of quartz and feldspar."

Bastin (Ref. 21) writes:  "Fragments of the wall rock are very
frequently found inclosed in the border portions of the granite
masses of Maine.  The phenomenon is less common in the case of the
pegmatites, but was nevertheless observed at several localities.
On the highest postion of Streaked mountain a number of patches
of schist of a few square yards in area were seen apparently en-
closed by pegmatites.  Small schist fragments are also inclosed
by pegmatites.  In the Boothbay Harden region, W. H. Emmons, of
the Geological Survey of the United States, who visited Mount
Mica a year later than the writer, when excavation had proceeded
farther, observed a few feet below the schist hanging wall, schist
fragments which appear to be wholly inclosed in the pegmatites.

The schist of these fragments made large angles with the schis-
tosity of the walls from which they had evidently been dislodged.
The pegmatites showed no bending of the minerals or other changes
in character near the fragments.  In the instance cited, the
schist fragments appear to have been caught up while the pegmatite
mass was still partly or wholly fluid and the density of the magma
was sufficient at least in the Mount Mica example to float the
fragments."

From the above it appears that at least some pegmatites were
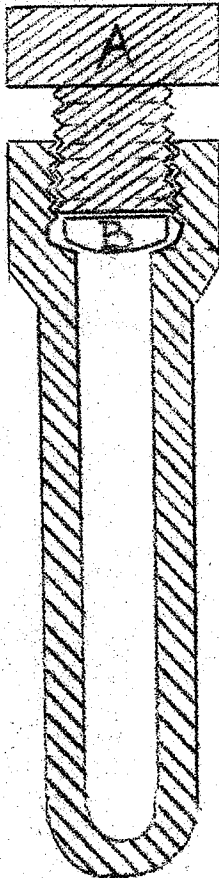formed from viscous magmas.

It has often been stated that pegmatitic magmas were so fluid

that they were able to permeate minute cracks and fissures in the
country rock. Gels are also capable of being squeezed into minute
fissures, although less readily, but can penetrate without dif-
ficulty the type of opening which pegmatites are found to fill.

IV. High Temperature Pressure Experiments on Silicic Acid Gel.

One of the first questions that naturally arises is whether
silicic acid gel can exist at the temperature of pegmatite con-
solidation. The limiting temperatures and pressures at which
silicic acid gelly retains its waters are uncertain (Ref. 22).
At ordinary pressure it looses most of its water at 100°C., but
a little remains up to 500°C., ignition by the blowpipe being
necessary to completely dehydrate this acid. At greater pressures
water would be retained at higher temperatures, because there is
a contraction of the total volume of silica plus water in the
formation of the gel. It therefore seems probable that it could
exist in pegmatites since alpha quartz is the normal
quartz of pegmatites, and consequently crystallization
of the quartz must have taken place below 575°C.
In order to verify this conclusion experiments on
silicic acid gel under high temperature and pressure
were carried out. Pure dialyzed silicic acid, of a
known water content, was placed inm a closed steel te-
st tube and heated under its own vapor pressure; the
temperature being noted by means of a thermocouple.
After heating for a definite length of time, the test
tube was chilled and the contents immediately removed
and analyzed for water. To insure that it was gel
water and not simply mechanically intermixed, the res-

idues from the experiment were first dehydrated in a dessicator, then the gel water was determined by ignition with the blowpipe.

The apparatus used consisted of a steel test tube, as shown in the diagram, closure being effected by means of a screw (A) which forced a cap (B), having a curved lower end, tightly over the curved lips (C) of the opening.

The results obtained on these experiments were tabulated in table I.

### Table I.

| | No. of Expt. | 1. | 2. | 3. | 4. |
|---|---|---|---|---|---|
| 2. | Amount of Silicic Acid Gel used in Grams | 8.8159 | 6.1250 | 6.7204 | 6.8271 |
| 3. | Percentage of Water in Gels. | 68.26 | 61.90 | 41.90 | 33.70 |
| 4. | Time heated in Bomb. | 2 1/2 hrs. | 24 1/2 hrs. | 26 hrs. | 1 week |
| 5. | Temp. of Bomb. | 700 ± 50°C | 650±50°C. | 650±50° | 650±50°C |
| 6. | Time in Dessicator. | 24 hrs. | 24 hrs. | 24 hrs. | 24 hrs. |
| 7. | Percentage Loss of Water in the Dessicator. | 11.01 | 18.08 | 15.82 | 14.02 |
| 8. | Percentage Loss on Ignition by the Blowpipe. (Gel Water) | 6.32 | 9.16 | 7.61 | 5.32 |

The figures in line 8 give the percentage of water retained by the gel at the temperatures and pressures of the experiments. It will be noticed that in experiment no. 4 the gel still contained 5.32% water although it had been heated for a week. Thus gels can exist at temperatures at least as high as 600°C under pressure

To chech whether drying in the dessicator was effective in removing all the mechanical water, the dehydrated silica obtained after the final blowpipe ignitions of experiments 3 and 4 was mixed with approximately 15% water and left in the dessicator to dry. Weighings were made each hour inm order to determine the rate of loss of the water. The results are given in table II.

### Table II

| Hours in the Dessicator. | Loss of Water from Residues of Expt. No.3 | Loss of Water from Residues in Expt. No.4 |
|---|---|---|
| 1. | 9.121 % | 8.704 % |
| 2. | 3.390 | 3.876 |
| 3. | 1.214 | 1.004 |
| 4. | .736 | .802 |
| 5. | .323 | .257 |
| 6. | .016 | .052 |
| 7. | .001 | .014 |
| 8. | .000 | .002 |
|  | 14.801 % | 14.711 % |
| Water at Start | 15.040 % | 14.890 % |
| Water Left | 0.239 % | 0.179 % |

The results indicate that practically all the mechanical water disappeared within 8 hrs. Therefore in the experiments where the residues from the bomb heating were left in the dessicator for 24 hours the mechanical water would have completely evaporated; and in addition the gel water would have probably been patially dehydrated. The figures in line 8, table I, then represent minimium values for the water content of the gels under the experimental

conditions.

The above values cannot of course, be strictly applied to ore deposits, as our knowledge of ore deposition is no quantitative. However, since the temperature of ore solutions is lower and the pressure of the overlying rocks greater than those used in the experiments, gels of veins would retain more water than the gels of the experiments. In brief, gels of considerable water content can exist in ore deposits.

V.  The Relation of Gels to Quartz Veins.

It has recently been advocated that silicic acid is the ancestor of vein quartz (Ref. 23);  and as these veins are known to grade into pegmatites which we also believe to have crystallized from silicic acid gel, the relation of gels to these two types of deposits offers problems which have much in common.  Recently, (Ref. 23), gelatinous silica in veins has been found.  In piercing the Simplon tunnel a gelatinous quartz vein was uncovered, and at the Great Australia Mine, Clonclurry, Queensland, silica in all stages from an ordinary liquid to veins which could be cut with a knife was discovered.  Levingx, (Ref. 23), has also reported the presence of gels in some of the veins of Tasmania.

Spurr, (Ref. 24) has recently put foreward the hypothesis that many high temperature quartz veins, or veindikes as he prefers to call them, have intruded into their present position as a viscous mass much after the manner of dike intrusions.  In support of this he cites numerous examples of angular inclusions of country rock and earlier minerals in veins, in such positions that they could not possibly have been previously connected.  He argues that the viscous veindikes caught up these fragments and held them suspended in their present position while crystallization  of the vein

material took place (ref.25). Only in one place does Spurr dwell
on the nature of the quartz veindikes and there he states that
silica jelly more nearly approximates to his conception of vein-
dikes than do hot spring solutions. Wevwish to extend this
opinion to a definite xtatement that quartz veins crystallized ✗✗
from silicic acid jelly;  and in support of this we note:

1.  The above mentioned examples of gelatinous silica in veins.

2.  The experiments recorded in this paper have shown that silicic
acid gel under pressure can exist at higher temperatures than
those pr evailing during the formation of veins.

3.  The gradation of quartz veins into pegmatites and the con-
sequent similarity of origin.

4.  The viscosity of the ore solutions, as indicated by the many
known examples of unconnected inclusions, points rather to a gel
than to a dilute solution.

5.  The concentric mineral rings which are often found in veins
and which occur in increasing distance between the bands from the
center outwards like the structures which can be reproduced by
rythmic precipitation from gels.

VI.  The Relation of Gels tomCarbonate Veins.

Certain unusual features of many carbonate veins are explicable
by assumíng crystallization from a gel. At Velardena (Ref. 27),
Mexico, Spurr found inclusions of galema and sphalerite in a cal-
cite vein;  and again at Georgetown he notes the presence of ang-
ular inclusions of blende in a rhodochrosite gamgue.  He accounts
for these inclusions by the assumption that these depssits were
intruded as viscous carbonate veindikes. Miller (Ref. 28) has
published an illustration of an ore specimen from Cobalt in which

there are at least twenty-five well defined bands of smaltite alternating with bands of calcite. Bastin (Ref. 29) remarks concerning this, "The most plausible explanation and the one recently adopted by a number of students of ore deposits as a tentative explanation for such phenomena, is the rythmic precipitation hypothesis developed by Leisegang." Bastin however makes no mention of a carbonate gel at Cobalt though rythmic precipitation assumes crystallization from a gel. The presence of inclusions of country rock in the veins of Cobalt have been pointed out by Whitehead (Ref. 30). Spurr Ref. 31), believes this indicates the viscous veindike nature of the solutions. Dendritic (Ref. 32) crystals of native silver and smaltite also point to a gel origin.

From this evidence we present the hypothesis that the Cobalt ores crystallized from a calcium carbonate gel.

In order to test this hypothesis experimentally, an attempt was made to synthesize the concentric banding of millerite and calcite. This association is found at Cobalt though not so common as the smaltite - calcite rings, but as the latter presented many experimental difficulties the former was chosen.

A calcium carbonate gelatinous precipitate was obtained by mixing saturated solutions of calcium chloride and sodium carbonate. The gel was then placed in the bottom of a U tube where it syneresized and the supernant liquid was poured off. Dilute ammonium sulphide was then added to one arm of the U tube and concentrated nickel sulphate to the other. In two weeks fine bands of millerite appeared and at the end of a month a series of ten very fine rings were visible. As it was impossible to photograph them a drawing is substituted.

Conc. $NiSO_4$.

Dilute $(NH_4)_2S$.

$CaCO_3$ Gel.

Bands of NiS.
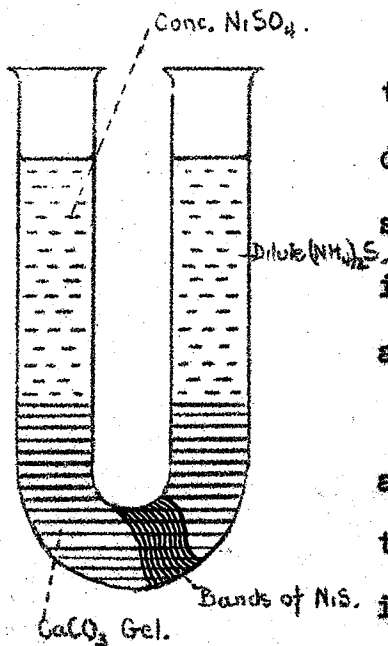
The combined evidence furnished by this synthesis, the inclusions of country rock and the dendritic crystals found at Cobalt, strongly support the hypothesis that the Cobalt ores originated by crystallization from a calcium carbonate gel.

As rhodochrosite and siderite veins also occassionally contain inclusions and mineral bands they may have originated as gels. Therefore the idea is extended to a generalization that all carbonate veins might have been initaded as gels

## VII. The Possibility of Other Gels in Ore Deposits.

As has previously been pointed put gels are simply precipitates formed from a solution where the value $\frac{Np}{Sp}$ exceeds 87,600. Most of the ore minerals are almost insoluble in water and even though their solubility in vein solutions may be considerably greater, yet it is conceivable that it is still so slow that even reactions between dilute solutions would produce them as gels.

The point we wish to emphasise is that certain structures such as banding of minerals, dendritic, aborescent and large crystals, and the presence of separated unconnected angular inclusions may be explained by crystallization from gels; and when these are present the possibility of a gel origin should be considered.

Every ore mineral is a theoretically possible gel.

## VII. Summary

The conditions for gel production are discussed and its similarity to ordinary precipitation pointed out. When the value $\frac{Np}{Sp}$

the degree of supersaturation, exceeds 87,600 a gel results.

The influence of various factors, such as temperature, pressure, composition, the presence of gases and mineralizers, on the texture of pegmatites, has been examined and found to be inadequate to explain such structures.

A hypothesis is advanced to show that during the consolidation of a magma, silicic acid is separated in the last stages of differentiation and rises to the top of the magma reservoir. Upon release of pressure the silicic acid intrudes adjacent fissures, forming pegmatites and veins.

Crystallization from such a gel favors the development of large crystals, as has been shown by several experiments. It also tends to form radiating, occassionally aborescent and dendritic aggregates, all of which are known in pegmatites, quartz, and carbonate veins.

High temperature pressure experiments on silicic acid gel show that it can exist at temperatures at least as high as $600^{\circ}C$ under pressure. Therefore it can exist in veins.

Quartz veins are held to have originated from silicic acid gels.

The concentric bands of millerite and calcite, found at Cobalt have been synthesized and a hypothesis put foreward that the ores of Cobalt crystallized from a calcium carbonate gel.

All vein minerals are considered theoretically possible in the gel form. When certain structures, which can be explained by crystallization from a gel, are found in ore deposits, the probability should be considered.

The relation of gels to ore deposits, as outlined in this paper, warrants further investigation; and it is hoped that in

the future  this work will be extended.

Appendix.

## A. Note on the Formation of Agates.

In a recent article on Retarded Diffusion and Rhythmic pre-
cipitation, Stanfield writes, (Ref. 33), "Agate structure has
been ascribed to the formation of Leisegang rings by diffusion
of solution throughn gelatinous silica. The discovery of gelat-
enous silica in the Simplon tunnel is of interest in this conne-
ction. On examáng certain agates the writer was struck by the
fact that many of them show bands which are equally spaced and
not at successively increasing distances as in the ordinary Leis-
egang rings."

"Thenwriter does not consider that agates in general can be
held to be produced by leisegang reaction. Out of a large number
examined but very few seem to be explicable only along these
lines, by far the greater number allowing of other explanations.
Each specimen of agate needs to be examined by itself, the his-
tory of each being of necessity a separate entity, and only com-
parable with others by an accidental reproduction of a similar
series of events."

In examing several agates we also find that many of them can-
not be explained by rhythmic precipitation, and we feel justified
in prexenting a short note to show that certain definite agates,
typical of various classes, are not formed from Leisegang re-
actions.

If agates were formed by the reaction of diffusing solutions
through gelatenous silicic acid, then concentric rings, from the
diffusing center should be formed. The distance between the ring

1



3



2



5
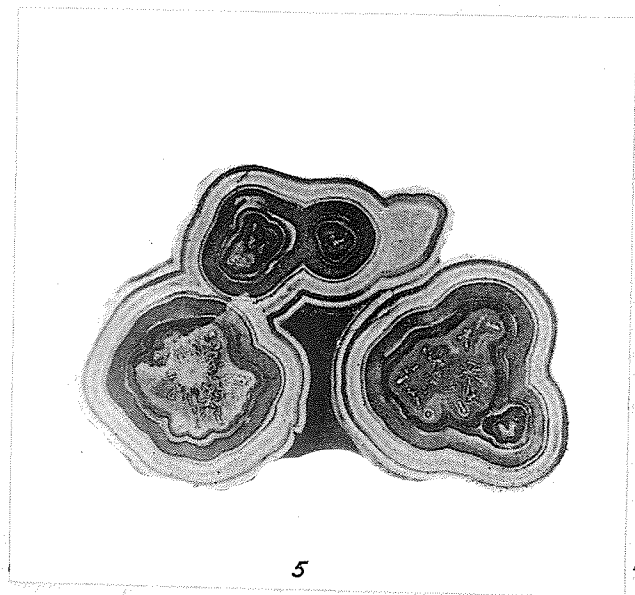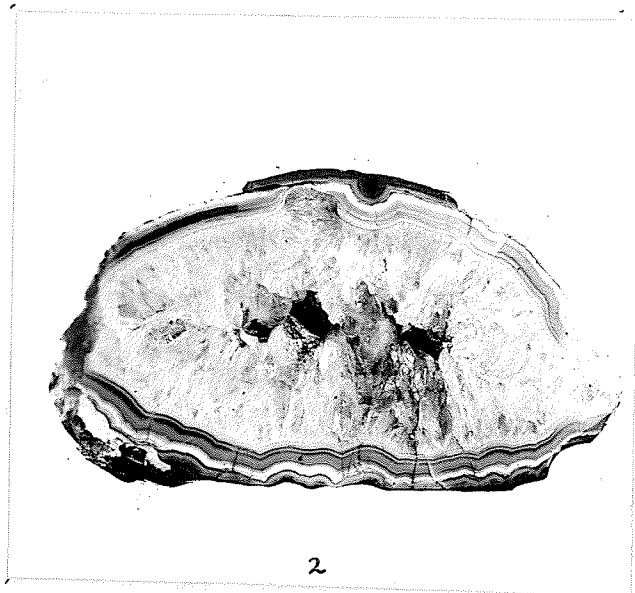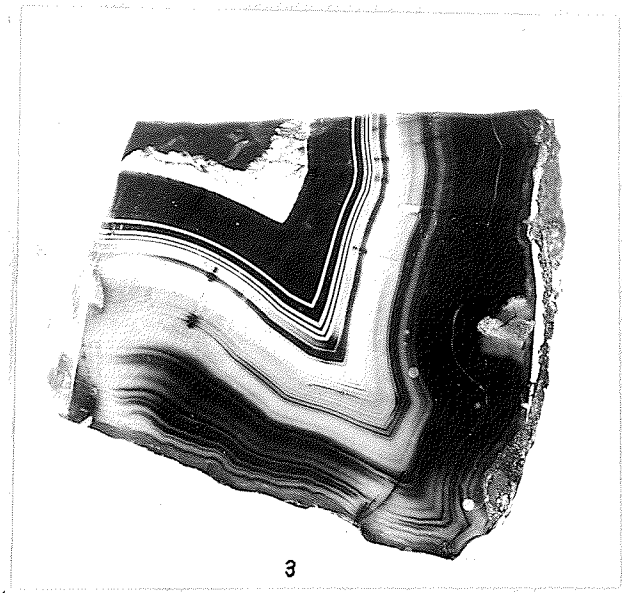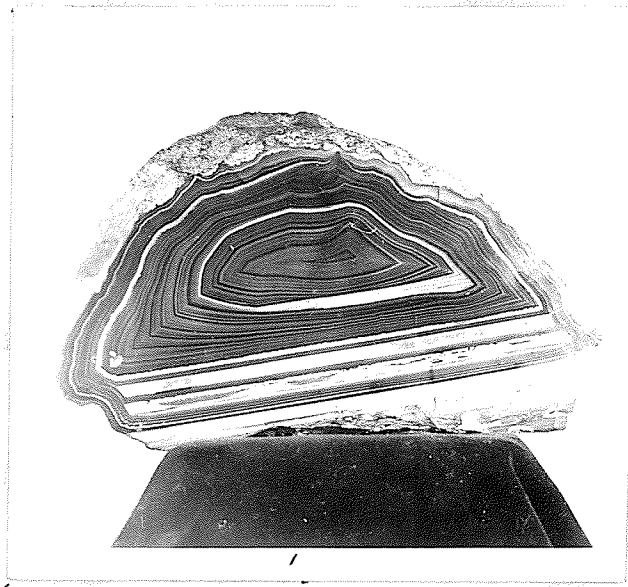
should increase outwards.  Individual bnds skould be of uniform width, since diffusion is equal in all directions of the gel. Also if diffusion has taken place from two or more points in the gel, lemniscates should be formed when the rings meet.

The following features in agates do not seem to coincide  with the above points.

In agates, as in No. 1, there are white bands which do not form a complete circle but which are between bands that do.

In many agates the distances between the bands are not successively increasing outwards from the center.  For example in No. 3 the first and second bright white bands are further apart than the second and third.

In other agates as in No. 2, bands are found at the edges, with very clear spaces in the center.  If formed from a gel there should be a series of rings from the center to the edge.

This agate also shows the solution cavity through which the solution entered.

In some agates the width of the individual bands vary as in No. 1 ring (a).

However agates with lemniscates are known as in No. 5, and theae owe their origin to rhythmic precipitation.

As these are representative types then most agates are formed by crystallization of successive solutions in a cavity.  A few however, are formed by reactions of diffusing solutions in silicic acid gel.

A tentative criteria for recognition of the origin of agates might be outlined as follows:

I. Agates formed by crystallization of successive solutions have some of the following features:

1.  Incomplete rings.

2. Individual abnds vary in width.

3. Distance between bands does not progressively increase from the center outwards.

4. The presence of solution cavities from which the solutions entered.

II. Agates formed by reactions ofmsolutions in gels have the following features:

1. Individual bands of uniform width.

2. The distance between the bands increase progressively from the center outwards.

3. The bands are complete.

The presence of lemniscates also indicate crystallization from a gel.

## Bibliography

1. Wo. Ostwald, (M. H. Fisher)., Handbook of Colloud Chemistry, p. 58.

2. Davies, Jour. Chem. Soc. 1865, 19, 71.

3. Ramsay, Jour. Chem. Soc. 1877, 32, 395.

4. Van Bemmelen, Zeit. Anorg. Chem. 1899, 20, 185.

5. Van Bemmelen, Die. Absorption 1910, 196, 214.

6. Holmes, Laboratory Manual of Colloid Chemistry, p. 432-448.

7. Washburn, Principles of Physical Chemistry p. 32.

8. J. B. Hastings, Origin of Pegmatites, Trans. Am. Inst. Min. Eng., 1908, 39, 104.

9. A. Harker, Natural History of Igneous Rocks, p. 294.

10. E. S. Bastin, The Pegmatites of Maine, U.S.G.S. Bull. 445, p. 27.

11. N. L. Bowen, The Later Stages of Evolution of Igneous Rocks, Jour. of Geology, 1915, 23 supplement, p. 66.

12. F. W. Clarke, Data of Geochemistry, p. 363.

13. H. N. Holmes, Formation of Crystals in Gels, Jour. of Phys. Chem., 1917, 21, p. 709.

14. H. N. Holmes, Formation of Crystals in Gels, Jour. of Phys. Chem., 1917, 21, p. 709.

15. H. N. Holmes, Colloid Laboratory Manual, p. 93.

16. Wo. Ostwald, (N. H. Fisher), Theoretical and Applied Colloid Chemistry, p. 108.

17. W. Lindgren, Ore Deposits, p. 763.

18. Williams, Gabbro in Neighboyrhood of Baltimore, U.S.G.S. Bull. 28, 1886, p. 25.

19. Fairbanks, 11th Annual Report, Calif. State Mining Bureau, 1890 - 1892, p. 94.

20. Blake, Tin Ores of South Dakota, Trans. Am. Inst. Min. Eng., 1885, 13, 695.

21. E. S. Bastin, Pegmatites of Maine, U.S.G.S. Bull. 445, 35

22. J. W. Mellor, Modern Inorganic Chemistry, p. 774.

23. E. Hatschek and A. Simon, Gels in Relation to Ore Deposits, Trans. Inst. Min. and Met., 1912, 21, 451.

24. Spurr, Ore Magmas, Chap. 2.

25. Spurr, Ore Magmas, p. 521.

26. Spurr, Ore Magmas, p. 519.

27. Spurr, Ore Magmas, p. 798.

28. Miller, Economic Geology 1917, 12, p. 224.

29. Bastin, Economic Geology, 1917, 12, p. 224.

30. Guild, Economic Geology, 1917, 12, p. 351, plate 18.

31. Spurr, Eng. and Min. Jour. Press, 1923, 116, 17, p. 709.

32. Whitehead, Economic Geology, 1920, 15, p. 116, plate 7.

33. Stansfield, Retarded Diffusion and Rhythmic Precipitation, Am. Jour. Sc., 1917, 43, 18.