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SOME POSSIBILITIES OF THE DEPOSITION
OF GALENA FROM COLLOIDAL SOLUTIONS

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Osborne Haydon

The possibilities for the deposition of ores from a colloidal state have only been generally recognized in recent years and this field furnishes interesting and almost unlimited possibilities for investigation. Workers in Geology, however, are not immune from the tendency shown by men in other fields in that as soon as a sound new idea is advanced, they work it to death. It was the fashion, not so many years ago, for doctors to take out an appendix for little or no reason, and the geologist must guard against this tendency.

Moreover, while it is doubtless true that colloid chemistry has progressed faster in the last ten years than any other branch of chemistry, it is equally true that practically nothing is known of the precise laws governing colloids and no reactions may be written for them. It is well, then, for the geologist to proceed with more than usual caution in this field.

The occurrence of free gold crystals in a ground mass of pure quartz has been always rather difficult to account for, but if we conceive of the quartz as having been in the form of a silica gel, and the gel having acted as a dialyzer to solutions carrying gold in the colloidal state; both of them subsequently crystallizing, or else the silica gel precipitating gold directly from molecular solution after the fashion of the common "Lead Tree", this occurrence is readily understandable.

Of this Holmes[†] says, "It is probable that gelatinous silicic acid was the ancestor of vein quartz, and by gradual de-

[†] H. N. Holmes; Lab. Man. of Colloid Chemistry, Chap. XIII. John Wiley and Sons.

hydration became hard silica rock. In the gelatinous medium, reactions took place under conditions favoring the formation of crystalline veins. For example, the reduction of gold salts produced crystals of gold, veining the gel, which later became quartz."

The often met collariform, botryoidal, or mammillary structures are explained on the ground that the minerals have crystallized from a gel, and that they still retain the outward appearance that the gel had before solidification or crystallization.

Before proceeding further it will be well to reach some common ground of understanding, and so a very short discussion of colloids will be given here, which is largely taken from Holmes' General Chemistry. He gives a short classification of colloids, only the first part of which we are interested in and which is reproduced here.

| | | |
|--------|-----------------------------|--|
| | (dispersed in another solid | (gold in ruby glass sodium in blue rock salt elements or compounds in some alloys |
| Grains | (| |
| | (dispersed in a liquid | (colloidal gold in water colloidal selenium in water |

The limit of visibility of the best microscope is about 100 micromicrons, while the size of the largest molecule approaches 1 micromicron; it is between these two limits that the colloidal realm ranges. There are at least three reasons why these particles - larger than a molecule, and which might therefore be expected to sink - stay afloat. They are: the Brownian movement, the presence of electric charges on particles,

and of protecting films around them.

Colloids are classified into suspensoids and emulsoids. Suspensoids are easily coagulated by very small quantities of electrolytes, and after coagulation may crystallize to form a "Metacolloid".

Svedberg^τ gives the following concerning the formation of colloids, "Colloids may be formed in two ways, differing in principle: by condensation or by dispersion. In one case matter is brought together within a smaller boundary surface than before; in the other case the matter is dispersed so that the specific surface is increased - - . Condensation processes are far more numerous and common than the dispersion processes.

"The primary condition for condensation is the existence of a system of higher dispersity than the one desired. - - The secondary condition for obtaining by condensation a disperse system with more than a merely ephemeral existence is the breaking off or retardation of the condensation process after having reduced the surface of the system to a suitable extent - - - ."

The centers of condensation may:

1 - Be present in the system before the condensation process sets in or be introduced independently of the processes that lead to condensation.

2 - Or they may be formed by the condensation process or in intimate connection with it.

The various forms of condensation processes are classified as follows:

- | | |
|---------------|--------------------------|
| 1 - Reduction | 3 - Dissociation |
| 2 - Oxidation | 4 - Double decomposition |

^τ The Svedberg: The Formation of Colloids; J. A. Churchill, London.

Peptization, or disintegration into colloidal particles through the action of some added chemical is the most common method of preparing colloids by dispersion.

"A distinction must be made between the primary degree of dispersion, which exists immediately after the carrying out of the colloid forming process, and the secondary degree of dispersion which is frequently brought about rather quickly in consequence of the aggregation of the primary particles, i.e., by coagulation. Further, one has to consider the tertiary degree of dispersion, which is the result of a process very slow compared with the two former processes, i.e., by crystallization."

"The primary degree of dispersion being commonly the highest, it is obvious that the methods of preparation in most cases aim at suppressing those processes which lead to secondary or tertiary degrees of dispersion. The chief methods of obtaining this are:

- 1 - Very low solubility of the disperse phase in the dispersion medium.
- 2 - Suitable (not too high) ion concentrations.
- 3 - Low concentration of the disperse phase.
- 4 - The presence of a protective colloid.
- 5 - Low temperature.
- 6 - The presence of some peptizing agent."

Thus it is seen that there must be some one or more of these favorable conditions present if a substance is to be transported in the form of a colloid. It would seem more probable that in the majority of cases, a substance transported over long distances should be in the form of a molecular solution, to be deposited either as a colloid or crystalloid, although this is not necessarily true in all cases.

Comparatively low temperatures are seen to be essential and in the case of gold quartz veins, this is easily realized ~~as the~~

as the quartz veins may be regarded as the aqueous end of a pegmatite vein or dike in which the temperature is low.

"Konigsberger^τ in his experiments has obtained chalcedony at 350 degrees C., which may be for the present regarded as the upper limit at which a silica gel can maintain itself."

In the article from which the above quotation is taken Lindgren gives an imposing list of minerals which he believes to be the result of colloidal processes. He groups these as: Amorphous gel minerals; Elements; Sulphides; Oxides; Carbonates; Hydrous silicates; Phosphates; Arsenates; Sulphates; and Vanadates. Sphalerite is included in the list of sulphides, but Galena is conspicuously absent.

He gives the following criteria of the colloidal state in minerals:

- 1 - Collo^{ro}form structure.
- 2 - Absorption of dyestuffs.
- 3 - Absorption of water, and the regular character of the dehydrating curve.
- 4 - Fibrous radial arrangement.
- 5 - Character of optical and physical properties.
- 6 - Variability of composition.

Regarding the character of solutions taking part in colloidal replacement, ^ΔBoydell says, "Generally speaking, it would seem that in more highly dispersed colloidal solutions,

^τ Centr. Mineral., Geol., Nos 11 and 12, 1906. Quoted from W. Lindgren, The Colloidal Chemistry of Mineral and Ore Deposits, R. H. Bogue, editor: Colloidal Behavior. MacMillan.

^Δ H. C. Boydell: Discussion of Metasomatism, Economic Geology. Vol. XXI, 1926.

and with the factor of geologic time taken into consideration, colloidal material can, in the larger openings at any rate, be transported to and from the site of metasomatic action, though not with the same facility or degree of availability in pores and open spaces of small size as molecularly dispersed material."

And further on, "The production of gels from dilute solutions or sols is an idea of recent growth and is due chiefly to Weiser^r, whose views have been summarized elsewhere^Δ in the following terms, "- - Weiser has quite recently pointed out that this (from supersaturated solutions) is not the usual condition of gel formation, and that the most stable gels are relatively dilute and are prepared by slow precipitation of dilute colloids or on mixing of dilute solutions where the degree of supersaturation is only small. The same writer considers that since finely divided particles that adsorb water strongly are essential in gel formation, the best method is the precipitation of a hydrous substance from colloidal solution, and he has prepared a number of inorganic gels in this way. He also refers to the importance of the time element and thinks that many more substances would form gels if given longer time."

In speaking of the solutions effective in colloidal transportation Tolman and Clark^γ say, "A broad application of the theory of transportation of colloidal sulphides in a dispersed con-

^r H. B. Weiser, Colloid Symposium monograph, Univ. of Wisconsin Chem. Dept., 1923, pp 38-61.

^Δ H. C. Boydell, Bull. Inst. Min. and Met. (London), Dec. 1924, pp 83-93.

^γ The Oxidation, Solution, and Precipitation of Copper in Electrolytic solutions and the Dispersion and Precipitation of Copper Sulphides from Colloidal Suspensions, with a Geological Discussion. C. F. Economic Geology Vol IX No. 6 1914.

dition is not possible under the earlier ideas that dispersion is prevented by slight elevations of temperature, by the presence of electrolytes in solution, and that colloidal solutions are suspensions of relatively large particles, and therefore cannot penetrate coarse filters or the pores of rocks. Up to date, attention has been directed chiefly to the colloids formed near the surface in the zone of weathering, and the transportation of dispersed sulphides by the deeper ore forming solutions has not been investigated. In the course of the experimental work, temperatures approaching 200 degrees C were employed, and under these conditions dispersion by hydrogen sulphide is increased. - - The idea that colloidal suspensions cannot pass through membranes and pores of rocks must be modified, and applies only to dispersions of large molecules, or particles such for instance as colloidal silica at ordinary temperatures and in alkaline solutions. Further, the idea that there is always a well defined gel state which later undergoes crystallization is by no means established. Crystallization may be practically simultaneous with precipitation of the dispersed matter."

Also, of the colloidal characteristics shown by veins formed at intermediate and moderate depths, the same authors in speaking of quartz veins of the "Mother Lode type" state that the colloidal character of the ore solutions becomes evident. The quartz, the gold, and most of the lead, zinc and copper sulphides are retained within the fissure, through which the silica cannot migrate.

That ore deposits are formed by colloidal processes seems to be a fairly well established fact, and the foregoing has been an attempt to summarize some of the criteria used in

determining whether or not the ore has been of colloidal origin, and also to present in a broad way some of the more necessary conditions to be met if a mineral is to be deposited in this manner.

Of the more common sulphides, that of lead is the only one not mentioned by Lindgren as being the result of colloidal processes. Anyone who has worked with lead sulphide realizes how easy it is to get an amorphous, jelly-like precipitate. It may be because of its position in the Periodic Table that lead does not have the same colloidal properties as the other common metals, but I think it quite possible that galena may have been formed as the result of colloidal solutions, but because of its tendency to so rapid and perfect crystallization, all outward appearance has been destroyed; also, as suggested above, there may have been no well defined gel state during the whole process.

It has been suggested that perhaps lead formed by the breaking down of radioactive substances might enter into the problem, but so far as I have been able to determine from the literature, radioactive lead and ordinary lead exhibit the same chemical properties, differing only in their atomic weights.

It was hoped that it would be possible to do some laboratory work of value, but because of two rather serious handicaps this hope was not realized; one was the lack of time, and the other was the lack of sufficient knowledge of chemistry to set about such experiment with any hope of success. However, I believe that if the work of Tolman and Clark on copper were to be followed with like experiments on lead sulphide, some interesting and valuable results might be obtained.

Some work was done in the laboratory. A gel made by dehydrating sodium silicate with acetic acid was placed in a U tube, and a solution of sodium sulphide in one arm of the tube, and of lead nitrate in the other. These were allowed to diffuse down through the gel, and lead sulphide was precipitated; the precipitate was not a uniform one, but was in bands, the "Liesegang Rings". A gel into which was introduced lead nitrate, before the gel set, and then sodium sulphide poured on top after setting, showed the same precipitation phenomena. One curious thing observed was that if the sodium sulphide was introduced into the gel, the gel became cloudy, although there was nothing present to cause the oxidation of sodium sulphide to free sulphur. It may just possibly be that the sodium sulphide is in a state of very fine colloidal suspension, and is coagulated by the electrolyte, acetic acid. The silica present may then act as a protective colloid preventing complete coagulation and precipitation.

The difference in osmotic pressure between the lead nitrate and the gel may be such as to prevent diffusion downward of the solution of lead nitrate. If, then, lead nitrate were poured on top there was no reaction observed. Several tubes were made up in which the lead sulphide was precipitated before the gel hardened. These and the others examined under the vertical illumination microscope for possible crystallization gave negative results; though perhaps not enough time was allowed before examination for the lead sulphide to crystallize.

There is no apparent reason why galena should not be transported in the colloidal state; lead sulphide is readily prepared in that form, and in so far as is known to the writer, the only reason it is not more generally included in the list

of metacolloids is the fact that galena shows such remarkably good crystallization, and rarely if ever the colloidal structure. Also, galena has a constant chemical composition; though there may be an exception to this in the case of the crystals of galena used in radio receivers; some crystals being very sensitive although what this sensitivity is due to is not quite clear. It generally shows good crystalline development except in the case of the so-called "steel galena" which is microcrystalline.

Tolman and Clark in the article noted above have recognized the colloidal character of the solutions depositing galena in veins of the "Mother Lode" type.

That so few of even the primary sulphides are homogeneous would seem a significant thing. Polished sections of apparently pure material, when examined under the microscope show them to be made up of a number of different minerals. While a great deal of this is easily explained by replacement of a secondary nature along cleavage cracks, a great deal of it is clearly contemporaneous with the predominating mineral. This has been explained on the ground that the two were deposited simultaneously and there the matter has been dropped.

Supposing, for the sake of argument, that we take the case of a piece of galena carrying sphalerite which shows up easily under the microscope, and which is contemporaneous with the galena. Now if the simultaneous deposition were from molecular solutions, would it not be reasonable to expect to find the sphalerite so minutely dispersed throughout the galena that the zinc present would only show up in a chemical analysis?

Would it not be more reasonable to believe that the two were carried along as colloidal suspensions, not passing through any well defined gel state but passing almost immediately into the crystalline condition? And because of some slight coagulation, causing a greater concentration of zinc sulphide molecules, there is, upon crystallization, the comparatively large patches of sphalerite in the galena?

Lindgren and Laughlin^r in their work on the Tintic Mining District of Utah, show some beautiful examples of banded jasperoid, which are due to rhythmic precipitation in a silica gel, which has later turned to chalcedony. Of this they say, "Such colloidal mass would be easily penetrated by electrolytes which by reaction with residuary solutions contained in the gel might easily produce such rhythmic precipitation rings as are shown in the Tintic Rock." Remembering the precipitation bands produced in the laboratory, which showed amorphous lead sulphide, these bands were quite likely amorphous or gel-like too, when they were first precipitated, crystallizing at a later time, and so have quite probably been in a colloidal state for a short time in their history.

The occurrence of lead and silver is wellknown, and the silver is quite often carried in the form of argentite in galena, often in patches large enough to be seen under the microscope. This argentite is clearly of the same age as the galena

^r Lindgren, W. and Laughlin, G. F.: Geology and Ore Deposits of the Tintic Mining District, Utah. p 156, and plates XVIII and XIX. Prof. Paper 107: U.S.G.S. 1919.

in a number of cases. Lindgren and Laughlin^τ show this particularly well in a section of polished ore taken from the Eagle and Bluebell mine, from the Tintic District.

Here again it seems difficult to understand how the argentite could occur in such large patches if it were the result of deposition from molecular solutions; rather, it would seem that they should be so closely intermingled that the silver present should only show up in a chemical analysis.

This difficulty is met with both in the case of the galena-sphalerite, and galena-argentite ores, if the solutions which deposited them are conceived of as not being particularly dilute, but more in the nature of Spurr's ore magmas. Then, the silver and lead sulphides could be carried along as colloidal solutions dispersed by some peptizing agent, as hydrogen sulphide which upon its escape caused the coagulation and precipitation of the two, either with or without the intermediate gel state before crystallization. This would explain the larger patches of argentite or sphalerite mixed in with the galena, because there would be many times as many molecules of the carried sulphide present in one spot, if the solution were colloidal, than if it were molecular.

^τ Lindgren W. and Laughlin G. F.: Op. Cit. Plate XXIX D.

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