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Title	STUDIES ON QUICKSILVER DEPOSITS WITH SPECIAL REFERENCE TO SOME CONSIDERATIONS ON THEIR GENESIS IN THE SOUTHWESTERN PART OF JAPAN.
Author(s)	UMEGAKI, Yoshiharu
Citation	Journal of science of the Hiroshima University. Ser. C, Geology , 1 (2) : 1 - 62
Issue Date	1952-03-25
DOI	
Self DOI	10.15027/52897
URL	https://ir.lib.hiroshima-u.ac.jp/00052897
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**STUDIES ON QUICKSILVER DEPOSITS
WITH SPECIAL REFERENCE TO SOME CONSIDERATIONS ON
THEIR GENESIS IN THE SOUTHWESTERN PART OF JAPAN.***

By

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(Received October 7th, 1951)

CONTENTS

Part 1.

(1) Introduction	1
(2) Quicksilver deposits in the southwestern part of Japan.	
(A) Formation in the inner zone.	
(B) Formation in the outer zone.	
(3) Some considerations on the genesis of quicksilver deposit.	
(A) Relations to the geologic structures and certain igneous activities.	
(B) Bringer of the ores.	
(C) Paragenesis of low temperature hydrothermal minerals	2
(D) Chemical property of mineralizing solution	7
(4) Summary	15

Part 2.

(1) Introduction	16
(2) Scope of the experiments	16
1. Spectroscopic analysis of the reagents	17
2. Practice of the synthesis	17
A. Experiments relating to quicksilver sulphides	17
B. Experiments relating to antimony sulphides	26
C. Experiments relating to arsenic sulphides	27
3. Solubility of the synthesized sulphides	27
4. Volatilizability of the synthesized sulphides	33
5. Specific gravity of the synthesized sulphides	34
6. X-ray analysis of the synthesized sulphides	35
7. Variation of PH-values in the media concerned	38
(3) Scrutiny of the experimental data	40
(4) Conclusion	48
Literature	50
Photo-plates	57
Figures	61

* Contribution from Geol. Inst., Fac. of Sci., Hiroshima Univ. No.15

Part I.

(1) Introduction.

With all the well-known fact that throughout the world there are more than twenty kinds of quicksilver-bearing minerals already discovered, it seems that only few of them deserve full scientific scrutiny or mining on the industrial scale. As shown in many researches so far made, nothing other than cinnabar associated with metacinnabarite or native quicksilver or with both, no matter whether it may be of primary origin or as placer, have ever been found out especially in our country. It also appears not negligible that, as can be anticipated from the writer's preliminary experiments or as was once suggested by Allen together with other authors, mercuric sulphides may not always be deposited merely as cinnabar or metacinnabarite but have rather numerous modifications yet to be determined.

On the other hand, even granting that the quicksilver minerals are formed as the final products precipitated at the latest stage of magmatic differentiation, it is still now a moot point whether or not the previous concepts relating to their genesis or to the process of mineralization may be justified intact. For instance, to what extent is it true that mercuric sulphides in question are dissolved in alkaline hydrothermal solution specifically containing alkali sulphide and, as a result, precipitate as sulphide minerals or rarely as native quicksilver? If such a limitation as to the chemical property of mineralizing solution and a view other than such a dualistic theorem as is attributable either to the alkaline or to the acidic state be established, can it be reasonably interpreted that certain minerals such as pyrophyllite, sericite, alunite and so forth believed to be rather secondarily produced in the acidic media are, as if from a single kind of solution, frequently accompanied with quicksilver minerals considered to be precipitated in alkaline state? Basing merely on a simple view so far stated, it is considerably difficult to construe these paragenetic relations with any other kinds of minerals having chemically antagonistic character.

Moreover, most of quicksilver deposits seem to have connection with certain geologic structures, especially those in the southwestern part of Japan. Their appearances surely point to a presumption that there may be a geologic relation between these deposits and tectonites being exposed near some sheared zones. This deduction, though it may hold good also in other kinds of ore deposits such as those of stibnite and others, appears most probable in the vicinity either of the Median Dislocation Line revealing a conspicuous contrast between each distribution of geology demarcated or of any other tectonic lines. Considering

the property of low temperature hydrothermal solution believed to have brought the quicksilver components, any other kinds of fissures of far smaller scale also must be taken up for inspection.

It also is still now a pending question to solve the problem as to the connection of ore genesis with igneous activity and, accordingly, the stage of formation, since, in spite of plentiful works so far made public, each case has been discussed dispersedly and, therefore, only the local explanations with more or less prejudicial observations lacking in universality have hitherto been given.

In the light of these considerations, the writer now wishes to report only the outline of his works which still leave so much yet to be clarified and are far from completion as it seems that, in so doing, a step can be taken toward the conclusion. He, however, regrets that most parts of his geological investigations, which will be published in another paper in the near future, must have been omitted owing to economic circumstances.

Emphasis must here be made as to the fact that the writer might have, but for a helpful advice from Dr. Prof. J. Takubo, been disposed to give up his enterprise because of a heavy blow he had suffered from the grievous accident at Hiroshima City on August 6, 1945 and knows no words with which to express fully his gratitude for the kindness and help afforded by the professor. At the same time, the writer has to extend his thanks also to Prof. A. Harumoto and Dr. Prof. J. Makiyama, from whose guidances he had benefitted to no small degree and to H. Miyako, by whose truthful assistance Part I of these investigations was completed.

(C) Paragenesis of low temperature hydrothermal minerals.

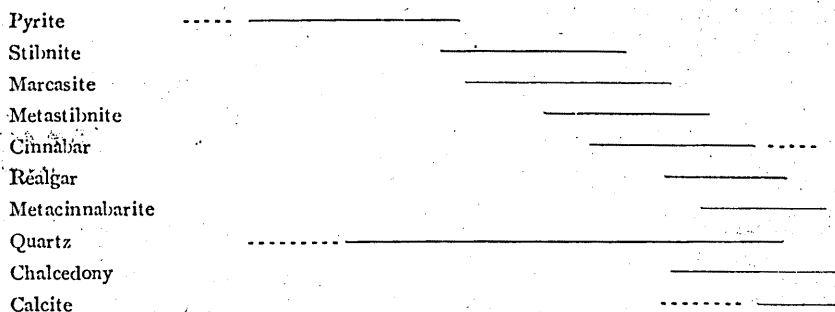
It is believed that some of the conditions suitable for the deposition of quicksilver minerals are to be clarified by means of pursuing the mutual relations among certain paragenetic minerals of low temperature hydrothermal property. Inasmuch as the reality, however, is that any quicksilver minerals other than cinnabar, metacinnabarite and native mercury have, notwithstanding numerous descriptions ever published, never been discovered in our country, reference must naturally be limited to the paragenetic relations of these three to any others.

As are recognizable in many deposits, quicksilver ores are used to be accompanied with certain ore minerals and gangues though their assemblage is not always invariable but different in each series of mineralization process even in the same deposit and have certain genetic relation to the formation of "Kuromono" and of "Rōseki." In some cases, it also happens that a sort of ore-carrying mineralizer precipitates the ores in question on one hand and alters the host rock to pyrophyllite or kaoline on the other. Formation of the latter may not pertain to such a category as has been deposited from the mineralizing solution

STUDIES ON QUICKSILVER DEPOSITS

but rather be ascribable to the secondary effects of hydrothermal alteration⁽²¹⁾ through the very solution.

The crystallization sequence of some minerals and their paragenetic relations have been shown only in each case. More noticeable is that a helpful suggestion for presuming the mineralization process or then-controlling conditions should be attainable from the inspection of an ideal diagram drawn by the combination of the results appeared in each preceding diagram. It is figured as in the following :



Among the minerals concerned, orpiment is often found mingled with realgar produced somewhat earlier than the former, though difficult to be compared with others because of its rarer occurrence. Calcite is considered to have been deposited later than gypsum as well as alunite rather in different series of the process. As regards fluorite, there is an only case showing its deposition at a stage almost similar to that of calcite. In this diagram, there are some pairs of dimorphic minerals believed to have been produced in antagonistic conditions. According to Stokes and others⁽²⁶⁾, pyrite is stable in alkaline state at ca. 150°~200°C. and marcasite, on the contrary, in acidic medium at a temperature lower than for the former. Dreyer⁽²⁷⁾ also permits the similar relation in that cinnabar is producible in alkaline solution at a temperature above 120°~150°C. and transformable to metacinnabarite with decrease of alkalinity and temperature. Far more important may be that there seems to be no need to persist exclusively in his view because Moltzau and Kolthoff⁽¹³⁾ also suggest that alkalinity is not a condition necessary for the formation of the reddish modification of mercuric sulphide. Although few of authors still seem to permit their genesis through sublimation, the writer ordinarily reaches the belief that mercuric sulphides have been derived from low temperature hydrothermal solution since most of other paragenetic minerals believed to have been formed in the similar state must be unstable at a temperature so high that the mercuric sulphide may sublime and such a extremely particular case where only mercuric sulphides recondense themselves independently on any other minerals can hardly be expected. The data given by Doelter⁽²⁸⁾

indicate that stibnite is dissolved into alkaline solution and may alter to meta-stibnite with acid but regain its original state when heated at 200°C. With regard to arsenic sulphides, it is chemically presumable that a modification probably identified to be orpiment can be precipitated only in strongly acidic state. Meta-cinnabarite of such a large size as is macroscopically recognizable is scarcely appeared but there is an example in Hinotani gallery of Nyū Mine in Mie Prefecture where comparatively well-crystallized specimens are found associated with cinnabar and realgar in a single vein as if they were certainly derived from quite a singular mineralizer. It seems necessary to refer to native quicksilver occasionally accompanied with cinnabar and in times occurring alone free from other ore minerals even in unaltered country rock. As is ascertainable in liparite at Tsuyama Basin, a hypothesis of its genesis deduced from the reaction of carbonate-including hot water may be given. Emmons⁽²⁹⁾ who proposes such a vertical zoning as includes cinnabar in the second zone and stibnite in the third, considering that the latter is produced in a deeper part or at a higher temperature than for the former. Some investigators⁽²⁹⁾ experimentally prove that the formation of native quicksilver can be due to the reduction of "ic" mercury to the metallic state by bituminous or carbonaceous matters. Dreyer, however, regards the periodical repetition of both dilution and reconcentration of hydrothermal solution as a sole requisite to deposition of native mercury in the extremely complicated system on one hand and approves also to some extent such a result of experiment, achieved by Broderick⁽³⁰⁾, that the native mercury is set free through the reaction of mercuric chloride solution with hydrogen sulphide or organic matters and with stibnite on the other. It seems uncertain that the reaction of stibnite results in the deposition of native mercury. For the present, no means other than distillation can industrially be adopted as the most efficient procedure to attain the metallic mercury. Nevertheless, it seems impossible to expect a high temperature from ore-bringing hydrothermal solution for the reason of paragenesis of other low temperature minerals or from certain experimental data; while the vaporizing temperature of mercuric sulphide is estimated at 580° C. and the vapor pressure of metallic mercury is considered to be 0.28 mm at 100° C. and 100 mm even at 260° C.⁽¹³⁾ Another important significance may be comprised in the fact that drops of native mercury are found impregnated, as if they were squeezed out from the country rock of tender property, in unaltered slate, for example, in the case of Yuki Mine, where no traces of any other paragenetic minerals are discovered. Whereas the theory as to the hypofiltration of hydrothermal solution may again hold good in this case, it is still a pending question whether or not an ordinary reducing action must in all respects be necessary to originate the native quicksilver.

From chemical point of view, it seems that, in each pair of minerals such as

STUDIES ON QUICKSILVER DEPOSITS

pyrite and marcasite, stibnite and metastibnite, and cinnabar and metacinnabarite; the preceding modification are considered to have been produced in alkaline state and the subsequent varieties, on the contrary, in acidic media at a temperature lower than for the former, though the relation to the state of solution is not congruous only in the case of antimony sulphides since stibnite is believed soluble even in alkaline solution. More noticeable fact revealed in the diagram is that one pair intersects with another and, in other words, a preceding modification in a pair of minerals is often partly co-existent with a subsequent variety in another pair; for instance, cinnabar is paragenized with marcasite in spite of their antagonistic chemical property, especially without any evidences affected by secondary agencies. Then, there is a sort of contradictoriness between the reality of their paragenesis and the chemical data denying it. This may readily be clarified, if a impudent presumption that all kinds of mineral other than pyrite might have been produced simply in acidic state is permitted.

In relation to the co-existence of some minerals primarily formed, consideration on the host rock affected by hydrothermal solution also may be a clue to clarifying the essential property of the very solution. Most parts of the alteration of country rock surely mean the genesis of minerals secondarily derived from the reaction between the rock concerned and the mineralizing solution and, hence, must be included in the subject pertaining to the paragenesis of mineral in a broader sense.

With reference to the variation of chemical or mineral constituents, several kinds of hydrothermal effects ⁽²¹⁾, ⁽³¹⁾ such as silicification or chalcedonization, kaolinization, muscovitization or sericitization, pyrophyllitization, chloritization, epidotization, albitization, propylitization, uralitization, alunization, carbonatization, analcitization and so on are mentionable. Certain bleaching effects spread over comparatively wide area seem salient especially in the case of the host rock impregnated with quicksilver or antimony ores. In spite of the fruitful investigations as to petrogenesis, descriptions are by chance destitute of any allusion to these effects, or, if any, only refer to the fact just as it is. This point may in times rather simply be interpreted in that the effect is considered to have caused only a marginal facies around the intrusive mass or to be due merely to a simple kaolinization or its like. The relation between the ore-carrying solution and the leucocratization of country rock has never been studied in full details. Although it is still questionable whether or not the bleaching effect ⁽²⁰⁾, ⁽²¹⁾ is always related to so-called kaolinization and what kind of agency may cause the very effect, the comparison of their chemical constituents seems to reveal that a sort of metasomatic action showing, for instance, both the increase in the amount of wates and the decrease in the amount of alkali and silica components may ordinarily result in kaolinization, sericitization and pyrophyllitization, etc., while

Baur ⁽²¹⁾ has proposed his view in a dry system concerning three components of K_2O , Al_2O_3 and SiO_2 . An example is appeared in the gypsum deposit of Wanibuchi Mine where the whole mass of ore body partly kaolinized and partly pyrophyllitized is enclosed by some layers of pyrophyllite and this evidently suggests that low temperature hydrothermal solution precipitates the ores on one hand and alters the host rock by means of its metasomatic effect on the other. It must also be noticed that this large quantity of gypsum impregnated in the whole mass and injected by some later veins of gypsum can never be expected but for the action of sulphuric acid-including mineralizing solution. This is the case where the bleaching effect is extremely conspicuous and the similar phenomena are recognizable also in almost all deposits of quicksilver or antimony ores.

Further discussion should be alluded to the relation between the genesis of quicksilver ores and pyrophyllitization. The late Dr. Kimizuka ⁽²³⁾ associates the pyrophyllitization appeared in "Rōseki" deposit of Mitsuishi Mine merely with the extraction of silicic acid mainly from the xenolithic shale by pneumatolytic action of fluorine and demonstrates it with his laboratory data or with the occurrence of fluorite veins in liparite in Tsuyama Basin. It is really dangerous to confine the action of fluorine to be pneumatolytic and to hold fast simply to analytical result of silica component. There is also a unreasonable plea in that an evidence has been obtained at Tsuyama Basin far away from Mitsuishi Mine. Fluorine can occasionally be held included even in water in certain well and, fluorite, too, is considered to be produced also in low temperature hydrothermal deposit. According to the writer's field observation, any fluorite veins are discovered nowhere in Tsuyama Basin, while, on the contrary, the cavity-filling or breccia-like crystal of fluorite are found accompanied with considerable amount of calcite in the agglomerate-like or brecciated liparite. Analogizing from the occurrence of quicksilver ores in pyrophyllitized liparite of Wake Mine near Mitsuishi, it is surely accountable to assume that "Rōseki" deposit in the surroundings of Mitsuishi, Yoshinaga and Wake districts are to be derived from low temperature hydrothermal solution. In view of these considerations, the deposition of stibnite in pyrophyllitized liparite in Kōne-mura and the formation of alunite veins in the very extrusive or alunitization of wall rock along some fissures appeared in Fujino-mura are also worthwhile to mention. The assemblage of these minerals in the same zone of pyrophyllite deposits can be the most helpful material with which to oppose the earlier theory of pneumatolysis and, at the same time, seems to be of due significance in determining the essential property of then-ascending mineralizer. The formation of gypsum in Wanibuchi Mine and of alunite in these pyrophyllite deposits shows that certain amount of sulphuric acid have been contained in low temperature hydrothermal solution at least at a

STUDIES ON QUICKSILVER DEPOSITS

certain stage. It consequently follows that the essence of pyrophyllitization or kaolinization seems to be redounded to the action of this acid and its effect can be chemically confirmed by comparing the amounts of silicic acid water, alumina and alkali components with their original quantities included in the rock concerned.

Silicification commonly believed to be a sort of hydrothermal alteration may sometimes play a role in the bleaching effect on the country rock but rather seems to signify simply the re-precipitation of silicic acid extracted by and included in hydrothermal solution since this component can be dissolved in alkaline medium and be re-precipitated with increase of acidity and anhydration. The similar process may be expected in the case of silicification, whereby the pores of the country rock are filled or cemented, thus partly resulting in leucocratization of the very rock. Despite of this presumption, the reality is that this agency is often ascertainable specifically in the case of quicksilver or antimony deposits but is not regarded as a characteristic of this kind of deposit.

As regards chloritization, it seems also doubtful to regard its effect as is ascribed merely to the action of alkaline solution. Because, as almost complete extraction of alkali and iron components as well as more or less subtraction of lime, magnesia, alumina and silica components from the chemical constituents of mafic minerals included mainly in igneous rock may result in chloritization, there seems no need of caring for whether the action may be alkaline or acidic if these results should thereby be brought. A proof for this view is surely revealed also in the fact that any other effects believed to be related to the acidity of the solution concerned are frequently observable associated with this chloritization. There are many cases where quicksilver ores are deposited in kaolinized or rarely pyrophyllitized country rock containing chloritized ferro-magnesian minerals.

(D) Chemical property of mineralizing solution.

It is indeed a well-known fact that there are famous deposits believed to have been precipitated by solfataric action as a sort of sinter of hot spring or geyser, for example, as shown in the case of Steamboat Spring and Sulphur Bank by Becker and others⁽¹³⁾. According to the writer's view, these very facts, on the contrary, seem to be a important factor opposing the idea which stands pat only on the volcanic activity. It is accountably evident that the action of slowly ascending or stagnant solutions is more effective than that of the instantaneously volatilizable gases for such solid body. On the other hand, a generally applied treatment may be that the mercury ores are distilled with some reducing or extracting reagents at a temperature of ca. 500° C. At Yuki Mine in Tokushima Prefecture, for example, the ores are calcined with their mother rock, that is, limestone whereby mercuric sulphide may be reduced to a metallic state after the

reaction ⁽³²⁾: $\text{HgS} + \text{CaCO}_3 = \text{Hg} + \text{CaS} + \text{CO}_2 + \text{O}$. During the process, pretty amount of the metal accompanying any other modifications is often liable to be expelled through the invisible passage between the retort and the condenser or even through the cooler itself. It can thereby be presumable that certain volatilizable varieties are expected to be attainable from these distillation-products. Allen and some authors ⁽¹³⁾ suggest that these matters are regarded as a variety similar to metacinnabarite. Even supposing that quicksilver components are brought out from a source in the depth in a gaseous state, it is still problematical simply to assume their recondensation accompanied by volcanic eruption about the fumarole. Geochemical data, on the contrary, indicate the probability that the quicksilver components included in a slowly ascending hot water result in precipitation with variation of physico-chemical conditions. As regards the chemical property of mineralizer or the conditions necessary for precipitating the quicksilver components as ore deposits, there have been several theories, among which those connected with the formation of complex salt by Becker ⁽¹³⁾ and later extended electro-chemically by Knox ⁽³³⁾ are most noticeable and Dreyer ⁽²⁷⁾ also affirms these views in his geochemical study. According to Knox's theory, mercuric sulphide is dissolved in alkaline alkali sulphide through the following reversible reaction: $\text{HgS} + \text{S}'' = \text{HgS}_2''$. The precipitation of mercuric sulphide depends thus merely upon the concentration of sulphide-ion. Since alkali sulphide also is reversibly hydrolyzable after the reaction:



the tendency of directing toward the left side of the equation or of increasing the concentration of sulphide-ion is accentuated with the alkalinity of the solution, while in a neutral or acidic medium alkali sulphide is more easily hydrolyzed owing to the consumption of hydroxide-ion, culminating in the increasing inclination toward precipitation of the mercuric sulphide. The summary of Knox's theory is that the mineralizing solution in question is to be of alkalinity since such chemical reactions as mentioned above are likely to appear in the process of low temperature hydrothermal mineralization and thereby the deposition of quicksilver ores is originated. In relation to this, it is also to be remembered that the reddish sulphide of quicksilver or surely cinnabar can be artificially synthesized with alkali sulphide in a perfectly sealed glass-tube kept in the air-bath at a temperature of ca. 100° C. almost overnight ⁽¹⁴⁾. On the contrary, blackish kind of mercuric sulphide seems more easily prepared by passing hydrogen sulphide gas through mercuric salt solution in the weakly acidic state than by reacting the very solution with alkaline alkali sulphide; the reaction in the latter case is so delicate that a slight variation of the conditions in the system keenly influences the stability of alkali sulphide and, accordingly, precipitation or solution of the sulphide in question.

STUDIES ON QUICKSILVER DEPOSITS

Judging either from the difficulty of obtaining the proper conditions for precipitating the reddish modification of quicksilver sulphide or from the poverty of such springs as were adduced by Becker throughout the world, it is questionable to emphasize the necessity of a special relation between alkalinity and deposition. Even though the scope is now definitely bounded by the property of ascending hot solution from the depth and momentous problems such as so-called magma itself, the mechanism of general mineralization process, heterogeneous distribution and aggregation of ores and so forth are excluded, why is it that the hydrothermal solution must be destined to be alkaline? In this regard, general belief is that alkali components are extracted from the wall rocks in the passageway of ascending solution or are due to the concentration of hydrogen-ion⁽³⁵⁾ in the depth. Nevertheless, is it possible to expect such a strength of alkalinity in native solutions and probable that an ideal alkalinity just sufficient to precipitate the stable mercuric sulphide through the interaction between certain salts and alkali sulphide is realized in nature? Although for the reason that silica component, after extracted from wall rocks by alkaline solution as soluble metasilicate, can be reprecipitated as colloidal state, those who agree with Knox's view support also the assumption of chalcedonization present in the telethermal deposits⁽³⁶⁾, it is to be considered that, as the result of decomposition of indissoluble silicates by reacting with certain kind of acid, considerable amounts of silicic acid may be brought out also as colloidal particles suspending in the solution and resulting in deposition.

As far as mercuric sulphide is concerned, the reaction-products between mercuric salts and alkali sulphide are rather unstable with a slight variation of conditions in the system and, accordingly, may be counted by various kinds. It therefore, appears considerably difficult to predicate that mercuric sulphide ore is always derived only from alkaline solution; in other words, the preceding equations skilfully suggested by Knox notwithstanding, the concept adhering simply to alkalinity of hydrothermal solution proves to be prejudicial. There may also be an important question in the respect that almost all opinions⁽³⁷⁾ ever given are merely dealt with the solubility of mercuric sulphide already deposited but not with conditions necessary for its deposition from original state. For attaining the decisive conclusion for the subject under discussion, any other factors such as paragenetic conditions of several low temperature hydrothermal minerals of primary origin are to be inspected. It, then, is of avail to investigate a pair of minerals believed to be produced in mutually antagonistic conditions and be co-existent with each other.

Either the carrier (definitely distinguished from the "ore-bringer") of the minerals in question or the property of hydrothermal solution has already been considered to some extent. However, the interpretation of the most essential

YOSHIHARU UMEGAKI

problem referring to the source of ore-forming metals still remains to be solved. Becker's presumption⁽¹³⁾ that metallic mercury originally included in granite itself was extracted out by the action of certain solution accompanying any volcanism may take the lead in the theory of ore formation but lacks in the accuracy of expression. When permitting parts of the theory of differentiation, it may be better simply to say that quicksilver as well as any other minerals were derived from magma reservoir. None the less, there are rooms for minute consideration on Locke's opinion⁽²⁴⁾ that "much granite is thought to be at the end of a metamorphic series that started in great part with marine sediments" may renew the interpretation about the genesis of ore deposits.

Apart from various presumption mentioned above, certain means directly to solve the problem on hand should be considered. As to this regard, the writer has once published his work⁽²⁵⁾ showing that sulpho-components such as sulphuric, sulphurous, thiosulphuric and polythionic acids, etc. or the salts related are included in some springs in our country. Moreover, another data obtained from quantitative analysis of a mineral spring appeared near Wake Mine in Okayama Prefecture are also given by the writer in Table 3 where the predominance of sulphuric acid is most remarkable.

Table 3

constituent	g./Kg.	constituent	g./Kg.
K_2SO_4	0.0040	H_2SO_4	0.5872
Na_2SO_4	0.0153	SiO_2	0.2222
$(NH_4)_2SO_4$	0.0013	KNO_3	0.0105
$CaSO_4$	0.3917	KCl	0.0059
$MgSO_4$	0.0421	NH_4Cl	0.0028
$FeSO_4$	1.5516	$AlPO_4$	0.0233
$Fe_2(SO_4)_3$	3.9758	Total	7.9633
$Al_2(SO_4)_3$	1.1296		

The similar fact is surely recognizable in that the mine water in the gallery of Shōkōzan pyrophyllite deposit in Hiroshima Prefecture also contains a considerable amount of sulphuric acid whereby the clothes are frequently apt to be worn away there. In these both cases, it is of significance that the acid in question may come partly from oxidation-zone but seems partly to be of primary origin.

On the other hand, Dreyer mentioned the effect of wall rock as a factor to influence the ionic equilibria shown by Knox. If any substances, whatever kind they may be or be they not even rock, have certain effects on conditions in the system, the precipitating action for quicksilver sulphides dissolved should naturally ensue. From either the geochemical or the ore-depositary viewpoint, much more

STUDIES ON QUICKSILVER DEPOSITS

important should be that the mutual relations between wall rocks and hydrothermal solution are investigated in details than that the conditions of solution, whereby the ores are thought to have been brought, are detected in a simple way inasmuch as, by combining the results obtained from the reaction between several kinds of rocks and certain solvents regarded as efficient to precipitate the ores with an actual occurrence of wall rocks altered by hydrothermal actions, the essential properties of hydrothermal solution and, in consequence, the genetic process of quicksilver deposits may partly be interpreted and retraced.

In conformity with these assumptions, the writer has accomplished some preliminary experiments, whereby the comparison of the effects of either acidic or alkaline solvents upon some kinds of rocks, the quantities of certain component extracted from each rock by the very reagents.

An outline of the experiments and the data obtained are given in brief as follows :

About 10 g. of rock specimen pulverized and accurately weighed are immersed in 100 c.c. of reagent held in Erlenmeyer flask, to which Liebig condenser is attached for the purpose of keeping the quantity and concentration of the contents invariable and are boiled for two hours : the reasons why the system should be kept at a boiling state are attributed to such considerations as : (a) Temperature factor as well as other conditions must be regulated to be as constant as possible in each experiment ; (b) Temperature elevated to a boiling point is believed similar to that at the latest stage of rest magmatic solution thought to have a connection with quicksilver deposition ; and (c) the velocity of reaction may thereby be promoted to an considerable extent ; while it seems that much more than two hours are not necessary since even five hours' reaction still yield nearly the same result as in the case of two hours' duration.

Deci-normal solutions of both sulphuric acid and sodium hydroxide, though their normality may probably be too much concentrated to bear comparison with natural solution, are provided for the experiments, as the reactions of these reagents may determine the direction of the theory regarding the state of solution and more or less quantities of the reagents in question are contained in spring water. Then, each specimen of rock used for the reactions has been selected among the samples collected by the writer in his field surveying and microscopically examined to be fresh. Although it is previously presumed that even the same sort of rock, if of different occurrence or locality, do not always give completely the same results, only the specimen of all kinds of rocks is provided for a series of reactions with a pair of both acid and hydroxide and the effects of both reagents on the specimen are compared with precision. When the two hours' reaction at a boiling state is finished, the condenser is removed from the flask and washed repeatedly. Washing water also is poured into the flask and, after being so kept as to settle the suspending particles, the whole solutions are filtered or separated from the suspensions by decantation ; the filtration, however, should be repeated, if need be. The filtrate obtained is then analyzed through a common method to determine the components extracted from each rock. The data are summarized in Table 4 wherein such components as are not so intimately related to the subject in question are excused.

YOSHIHARU UMEGAKI

Table 4 (a)

Kind of rock	Sample in g.	Extracted amount in g. (by H ₂ SO ₄)		
		SiO ₂	Fe ₂ O ₃	Al ₂ O ₃
1. Biotite granite	10.0061	0.0309	0.1168	0.0066
2. Felsitic granite	10.0018	0.0353	0.1007	0.0421
3. Granite porphyry	10.0053	0.0438	0.1898	0.0272
4. Hornblende andesite	10.0150	0.0560	0.0120	0.0747
5. Liparite	10.0006	0.0418	0.1516	0.0184
6. Tuff	10.0080	0.0473	0.0405	0.0368
7. Schist proper	9.9825	0.0442	0.0681	0.0195
8. Sandstone	10.0019	0.0327	0.0575	0.0382
9. Carbonaceous shale	10.0469	0.0150	0.0628	0.0580
10. Inkstone	10.0006	0.0728	0.0146	0.0038
11. Limestone	9.9991	0.0458	0.0111	0.0239

Table 4 (b)

Kind of rock	Sample in g.	Extracted amount in g. (by NaOH)		
		SiO ₂	Fe ₂ O ₃	Al ₂ O ₃
1. Biotite granite	10.0029	0.0465	0.0074	0.0533
2. Felsitic granite	10.0418	0.0439	0.0006	0.0162
3. Granite porphyry	9.9976	0.0439	0.0035	0.0378
4. Hornblende andesite	10.0420	0.0767	0.0259	0.0160
5. Liparite	10.0036	0.0585	0.0020	0.0085
6. Tuff	10.0065	0.0274	0.0023	0.0010
7. Schist proper	10.0042	0.0476	0.0320	0.0236
8. Sandstone	10.0079	0.0531	0.0292	0.0384
9. Carbonaceous shale	10.0004	0.0784	0.0220	0.0133
10. Inkstone	10.0040	0.0554	0.0041	0.0182
11. Limestone	10.0072	0.0334	0.0069	0.0142

The respective localities of the rocks used in the above-stated experiments are as follows :

1. Biotite granite : Saijo Basin, Hiroshima Pref.
2. Felsitic granite or, strictly, hornblende-biotite granite : Notsuharu-mura, Ono-gun, Oita Pref.
3. Granite porphyry : Miyoshi Basin, Hiroshima Pref.
4. Hornblende andesite : Kawazoe-mura, Kitaamabe-gun, Oita Pref.
5. Liparite : Fujino-mura, Wake-gun, Okayama Pref.
6. Tuff : Wanibuchi-mura, Hinokawa-gun, Shimane Pref.
7. Schist proper : Nyu-mura, Kitaamabe-gun, Oita Pref.
8. Sandstone : Sacki City, Oita Pref.
9. Carbonaceous shale : Ditto.
10. Inkstone : Nishiichi-machi, Toyoura-gun, Yamaguchi Pref.
11. Limestone : Hetsugi-machi, Oita-gun, Oita Pref.

Because of the scarcity of the data adduced, any decisive or general conclusions cannot be reached from Table 4, while it, however, seems that some of the results are, in a sense, suggestive and indicate somewhat significant facts and the following interpretation may probably be possible.

It is obvious that every rock is at a same time affected by sulphuric acid as well as sodium

STUDIES ON QUICKSILVER DEPOSITS

hydroxide, although the reactions in each case must be essentially distinguished from each other. The decomposition of rocks is mainly ascribable to the action of the acid on one hand and the extracting effect on certain components seems to come from that of the hydroxide on the other. More detailedly, it runs as follows :

(a) Silicic acid may be dispersed as suspensions or colloidal particles leached through the filter paper due to the decomposition of rocks by acid³⁰⁾ and dissolved in solution as soluble metasilicate made available by the effect of sodium hydroxide. As far as the apparent quantity extracted is concerned, there is not so conspicuous a difference as is commonly expected between the influence of acid and that of hydroxide, respectively, on silica. From these results only, such view that chalcidization or silicification accompanying deposition of quicksilver sulphides is caused not only by alkaline solution but also by acid may be justifiable and, in consequence, may overturn the previous opinions relative to the genesis of quicksilver deposits that they are originated merely by alkaline solution.

(b) In the case of iron components, the result of analysis indicates that a greater amount of them is likely to be extracted from each rock or be more easily dissolved into solution by acid than by alkaline solution. It must here be added that certain amount of ferrous iron assumed as included in some kinds of rocks is taken in the total of ferric oxide and that special alteration, such as chloritization and its like, of the specimen is scarcely confirmable. These data have a significance with reference to the bleaching effects on rocks and perhaps to the genesis of quicksilver deposits. It is because that rocks colored by containing ferro-magnesian silicates and for any other reasons are, more so than not, faded due to the extraction of iron components by the decomposing action of acid. The eventuality is that, as a result of alteration spread over a comparatively wide area by this agency, the country rocks impregnating epithermal ores frequently show the appearance of alaskite, felsite or aplite and similarly bleached lodes or veins are macroscopically also likely to be confused and often mistaken for aplite dyke of primary origin.

(c) As for the extracted amount of alumina, no special inclination can be derived from the above data. Owing to its amphoteric character, some quantity of aluminium components may be dissolved both in acid and in alkaline solution and, accordingly, it seems hardly possible to find the difference between the actions of the two but is only sure that the increase or decrease in the amount of alumina as well as any other components, such as alkali earths and alkali metals, is apparently an important factor pointing to the solution of the question on hand and, at the same time, is intimately connected with pyrophyllitization or agalmatolization frequently recognizable in low temperature hydrothermal deposits.

Basing merely on these considerations concerning the extracting actions of special reagents of a definite normality, it may be impossible to reach a perfect clarity as to alteration of rocks affected, whereby a part of the property of hydrothermal solution may be indirectly induced. Because, for instance, there arises a question in the respect that no reference has been made with regard to chloritization of country rocks but this kind of alteration is commonly used to be observable also in the rock kaolinized by the action of acid. Furthermore, as alluded to already, it should be remarked that the genesis of sulphate minerals such as alunite, gypsum, barite and so forth, though some of them must be of secondary origin, impregnated in epithermal deposits are to be related to the action of sulphuric acid.

Be it so, the subject is now to be taken into account in the direct relation to the genesis of quicksilver ores. With all necessary things under considerations, the writer, concentrating his attention on condition to realize the natural phenomena as fully as possible, has undertaken some qualitative experiments, especially those pertaining to quicksilver sulphide.

Then, a deci-normal solution of mercuric chloride, a normal sulphuric acid, a normal solution of

YOSHIHARU UMEGAKI

sodium hydroxide and diluted solution of sodium sulphide are prepared and variously combined to cause the mutual reaction to one another in the system held at a room temperature.

1st step : On the condition that 5 c.c. of sulphuric acid are added to 5 c.c. of mercuric chloride solution, no changes are observable. 2nd step : By adding 1 c.c. of sodium sulphide solution to the above solution, milky whitish amorphous precipitates are formed. This seems to signify the separation of free sulphur derived from decomposition of sodium sulphide by means of acid. 3rd step : When some more c.c. of sulphuric acid are added to the above turbid solution, no changes may yet be observed. 4th step : Addition of another 5 c.c. of sodium hydroxide solution to the above solution reveals no remarkable reaction yet. However, as soon as more quantity of the very alkaline solution is added, thereby to exceed the neutral state, the color of turbidity changes from milky white to bright orange. 5th step : When slightly less than 5 c.c. of sodium hydroxide solution are added to the solution obtained by mingling 5 c.c. of sulphuric acid with 5 c.c. of mercuric chloride solution in the same manner as in the 1st step, it seems due to consumption for simple neutralization that no changes occur, whereas addition of a little more quantity of the former results in the formation of orange-colored colloidal precipitate. According as the very alkaline solution increases volume, precipitates become more and more voluminous, but if the total quantity of the added solution exceed ca. 7 c.c., the increase in the volume of precipitates seems to cease. From an inspection of the yellowish color, the formation of mercuric oxide or its like may be presumed but the volume is too enormous to allow comparison with concentration of mercuric chloride in the solution. 6th step : With sulphuric acid just equivalent to sodium hydroxide added in 5th step, orange-colored precipitates are almost completely dissolved and, at last, the solution of slight turbidity is only obtained. 7th step : When a little more than 2 c.c. of sodium hydroxide solution are added drop by drop to 5 c.c. of mercuric chloride solution, amorphous substances are precipitated. By adding 3~5 c.c. of sulphuric acid to the former solution, the precipitates are dissolved and slightly turbid solution is obtained. 8th step : If 10 c.c. of sodium sulphide solution are added to the mixed solution holding the yellowish precipitates produced in the same process as in 7th step, the precipitates in the solution is obtained. 9th step : Adding 5~7 c.c. of sulphuric acid to the above solution, reprecipitation of yellowish amorphous deposits begins to take place.

Although the original state of quicksilver brought about by any agency from any source of the depth is not easily presumable; the reason why the chloride has here been used is merely that this salt as well as the nitrate may be readily obtained as a dissolved state. Moreover, as to the chloride, Allen and others¹⁰⁾ once pointed out the possibility of deposition of mercuric sulphide after its reaction with thio-sulphate in acidic state.

The result of the experiment can be summarized as follows ; (1) The chloride may be co-existent with sulphuric acid. (2) With addition of sodium sulphide, its reaction with sulphuric acid becomes obscure, because of decomposition of the sulphide. (3) In alkaline state, the chloride may yield certain yellowish or orange compounds regarded as oxide or its like. (4) In neutral state, even if it is one subsequently made, the chloride may come into solution. (5) Uncertain compound precipitated in alkaline medium may be dissolved by addition of sodium sulphide.

After all, as far as the effects of acid and of alkali hydroxide on the solubility of the chloride are concerned, it seems difficult to deduce, simply from the preceding result, which is more effective. As a matter of fact, however, this should be just a reality and far more significant is that the result suggests the impossibility of adhering only to the alkalinity of solution.

STUDIES ON QUICKSILVER DEPOSITS

(4) Summary

(1) Quicksilver-bearing minerals occurring in the southwestern part of Japan are, for the time being, limited only to cinnabar, metacinnabarite and native metal.

(2) Quicksilver components are likely to be contained as ores in almost all of low temperature hydrothermal deposits, no matter to what kind they may belong.

(3) Many evidences pointing to contradictoriness of an old idea that cinnabar must necessarily be precipitated merely in alkaline solution are available. Inspection of the relationship between quicksilver ores and other paragenetic minerals suggests that any discussion based on the state of the solution alone is not hitting the mark.

(4) Most of the bleaching effects appearing in the country rock of quicksilver deposit must surely be attributable to the action of acidic solution wherefrom the ores also are presumed to have been precipitated.

(5) It has frequently been assumed that there were a special relation between certain tectonic lines or igneous activities appeared along or near the median line and deposition of quicksilver ores but these phenomena reveal nothing but a characteristic feature of general low temperature hydrothermal deposit produced along the tectonically weak zones, whatever they may be.

(6) From the mode of occurrence of ores in question and the correlation among certain kinds of igneous rocks, such a category regarding the stage of ore formation as is connected with the post-activity of biotite granite or liparite in earlier Tertiary may be derived with an only exception in the case of Ogata where, however, nothing can now be obtainable with regard to the ore genesis.

(7) It seems still to be a pending question how to expand Lock's hypothesis as to granite and ore and to connect it with the deposition of quicksilver ores or rather of any other minerals.

Part 2.

(1) Introduction.

As is widely known, it seems that as to the genesis of cinnabar many of investigators have hitherto taken into account merely the opinion suggested by Knox, Dreyer and others who believed the process, through which the mercuric sulphide mineral should result in the precipitation by decomposition of its complex salt dissolved in alkali sulphide in alkaline state with the variation of condition. This view, however, indicates only the facility of solution of the sulphide into alkaline medium but gives no evidence for the possibility of its genesis itself. The writer also has recently obtained the reddish mercuric sulphide only by heating the blackish modification enclosed in the sealed glass-tube at ca. 550° C. and ascertained, at the same time, its transition to cinnabar by means of x-ray analysis. Since the subliming point of mercuric sulphide, however, has already been estimated at ca. 500° C. and it is sure, too, that the mineral in question must not be producible solitarily by the simple dry-reaction but rather in far more complicated media, this synthetic procedure also is considered almost of no significance from geochemical or ore-depositary point of view. On the basis of the results obtained from field observation and microscopic examination, on the other hand, the writer has reached a sort of confidence that the stress of investigation as to the genetic origin of the mineral concerned must be laid not only on the manipulation for synthesis but also on the conditions of such surroundings as are naturally expected or the media similar to the state of nature and specifically on the prolongation of time for reaction, and thus attained a conclusion quite different from the previous conceptions already given by some authors in the light of consideration on the paragenesis of certain kinds of minerals and on the so-called hydrothermal alteration of country rock. Accordingly, several kinds of laboratory works, though they seem, at a glance, to have been a sort of trial-and-error method, have been proceeded along a special line in order to prove his assumption. The results obtained from these experiments were partly examined by x-ray analysis, as to which the writer here must express many thanks for the kindness of Dr. H. Tazaki and his assistants who have for a long time admitted the use of the apparatus in their laboratory. More thanks must be dedicated both to Dr. Prof. J. Takubo who has constantly given the writer both advice and guidance necessary for the whole investigation and to M. Yukimori whose continuous assistance extraordinarily contributed to the works.

(2) Scope of the experiments.

The experiments were put in operation with regard to the subjects, such as :

STUDIES ON QUICKSILVER DEPOSITS

1. The spectroscopic examination of purity of the reagents provided for the experiments:
2. The synthetic experiments:
3. Solubility of the synthesized sulphides:
4. Volatilizability of the synthesized sulphides:
5. Specific gravity of the synthesized sulphides:
6. Determination of their crystal structures by means of x-ray diffraction:
7. Variation of pH-values in the media concerned.

As a matter of course, the works performed are mainly related to the quicksilver sulphides but a part of them, to the other sulphides such as those of antimony and arsenic for the purpose of clarifying the question of whether or not the conditions suitable for the former case are applicable to the synthesis of the latter two.

1. Spectroscopic analysis of the reagents.

In special consideration of the study made by Dreyer⁽²⁷⁾ who ascribed the color of cinnabar to the kind and quantity of the impurities involved, the reagents used for the process of experiments, that is, the powder of mercuric chloride, the solution of antimony trichloride, the powder of arsenous oxide and the solution of arsenic chloride were carefully analyzed through a usual spectroscopic manipulation, the results of which are shown in Plate 52 where the remarkable amounts of impurities were scarcely found in the case of mercuric chloride and arsenous oxide but few, in antimony chloride.

2. Practice of the synthesis.

A. The experiments relating to quicksilver sulphide.

- 1) Blackish kind of mercuric sulphide was prepared by passing hydrogen sulphide gas through 10 c.c. of the saturated solution of mercuric chloride at a room temperature.
 - a) When each 10 c.c. of hydrochloric acid of various normality, such as 10 N, 1 N, 0.1 N, 0.01 N and 0.001 N (similar to other cases if no references were added), was mingled with the solution obtained above respectively, no change were observable on the color of the precipitate.
 - b) When each 10 c.c. of sodium hydroxide solution of various normality was added to the same solution, no changes were observable on the color of the precipitate, the dissolution of which was notable only in the case of 10 N and 1 N.

It must be remembered that the state of the whole solution became alkaline with 10 N and 1 N hydroxide solution, almost neutral with 0.1 N and acidic with 0.01 N and 0.001 N.
- 2) a) When hydrogen sulphide gas was introduced into 10 c.c. of the saturated solution of mercuric chloride previously mixed with the same quantity of hydrochloric acid of various normality and was foiled for some minutes, greenish yellow-colored precipitate was produced merely in the case of 10 N of the acid and blackish one, in other cases.

YOSHIHARU UMEGAKI

- b) When hydrogen sulphide gas was passed through 10 c.c. of the saturated mercuric chloride solution previously added with the same quantity of sodium hydroxide solution of various normality and was boiled for some minutes, the blackish precipitate maintained in the solution was completely dissolved into greenish brown-colored solution only by addition of 10 N hydroxide solution.
- 3) The black-colored precipitate produced by passing hydrogen sulphide gas through the saturated mercuric chloride solution at a room temperature was enclosed in the glass-tube respectively with pure water, a drop of concentrated solution of sodium sulphide and a drop of 10 N solution of sodium hydroxide. Then, each of them was heated in the air-bath at $95^{\circ}\sim 100^{\circ}\text{C}$. for forty hours. In the case of sodium hydroxide, the precipitate was completely dissolved but, in other cases, no changes were recognizable.
- 4) a) 10 c.c. of sodium hydroxide solution of each normality and then the same quantity of equivalent solution of hydrochloric acid were added to the saturated solution of mercuric chloride. When hydrogen sulphide gas was introduced into each solution thus obtained, the blackish precipitate was produced in each case.
- b) 10 c.c. of hydrochloric acid of each normality and then the same quantity of equivalent solution of sodium hydroxide were added to the saturated solution of mercuric chloride. When hydrogen sulphide gas was passed through the solution thus obtained, the results were similar to the case of a).
- 5) a) The black-colored sulphide deposited by passing hydrogen sulphide gas through the saturated solution of mercuric chloride, when it was boiled with 0.01 N solution of sodium hydroxide, became to show somewhat brownish tinge.
- b) No changes were observable on the tinge of the same sulphide, even if it was boiled with less than 1 N solution of hydrochloric acid.
- 6) a) When hydrogen sulphide gas was introduced into the saturated mercuric chloride solution mixed with less than 1 N solution of sodium hydroxide, the black-colored sulphide was deposited. No changes were observable, even if the precipitate was boiled.
- b) When the saturated mercuric chloride solution was previously mingled with hydrochloric acid instead of sodium hydroxide, the blackish precipitate invariable only by boiling was similarly produced.
- 7) When hydrogen sulphide gas was introduced into the saturated solution of mercuric chloride at a boiling temperature, the blackish sulphide was deposited.
- a) With addition of less than 1 N solution of hydrochloric acid, no changes were recognizable on the very precipitate.
- b) With less than 1 N solution of sodium hydroxide, the results were similar to the case of a) but the precipitate was completely dissolved in 10 N solution.
- 8) Hydrogen sulphide gas was introduced into the saturated solution of mercuric chloride previously mingled with variously concentrated solution of hydrochloric acid and sodium hydroxide at a boiling temperature.
- a) With another addition of 10 N hydrochloric acid, the color of the precipitate produced varied from yellow to greenish yellow, grey and black in the course of time. In the case of other normality, the black-colored sulphides were similarly obtained.
- b) With 10 N solution of sodium hydroxide, greenish yellow solution was attained. In other cases, the black-colored sulphides were deposited.
- 9) a) When the solution obtained in the case of 7) b) was neutralized with the same quantity of equivalent solution of hydrochloric acid and boiled, the black-colored sulphide was reprecipitated.
- b) When the solution obtained in the case of 8) b) was neutralized with the same quantity of equivalent solution of hydrochloric acid, the brownish black-colored precipitate was obtained merely in the case

STUDIES ON QUICKSILVER DEPOSITS

- of 0.1 N but no changes were observable in other cases.
- 10) When hydrochloric acid and then the same quantity of equivalent solution of ammonium hydroxide were added to the blackish sulphide precipitated by passing hydrogen sulphide gas through the saturated mercuric chloride solution at a room temperature, the results were quite similar to the case of the reaction with sodium hydroxide.
 - 11) When each 10 c.c. of ammonium hydroxide solution of various normality was added to the same quantity of the saturated mercuric chloride solution at a room temperature, egg-white-like precipitates were produced in the concentration of more than 0.1 N. The passage of hydrogen sulphide gas through the solution maintaining these precipitates varied the color of the latter into black but the solution was still colored with yellowish tinge in each case of more than 0.1 N solution of ammonium hydroxide.
 - 12) When each 10 c.c. of ammonium hydroxide solution of various normality was added to the same quantity of equivalent solution of hydrochloric acid including the blackish mercuric sulphide produced through a ordinary process, the very precipitate remained intact with mere exception of the case of 10 N wherein its color varied from yellowish to black.
 - 13) When ammonium hydroxide solution of various normality was added to the solution holding the blackish sulphide deposited through a ordinary process, no changes were observed on the very precipitate.
 - 14) If the experiments in the case of 10) to 13) were repeated at a boiling temperature, the results obtained were scarcely distinguishable from those attained in the preceding cases.
 - 15) a) When variously concentrated hydrochloric acid solutions maintaining the blackish mercuric sulphide were neutralized with ammonium hydroxide respectively and boiled for some minutes, no remarkable changes were recognizable on the precipitate.
b) When ammonium hydroxide solutions containing the sulphide were oppositely neutralized with hydrochloric acid, the results obtained were similar to the case of a).
 - 16) a) When hydrochloric acid solutions of various normality and then the same quantity of equivalent ammonium hydroxide solutions were added to the saturated mercuric chloride solution and hydrogen sulphide gas was introduced into them at a boiling temperature, greenish black-colored precipitate in the case of 10 N, greyish black one in the case of 1 N and blackish sulphides in other cases were obtained.
b) When ammonium hydroxide solutions of various normality and then the same quantity of equivalent hydrochloric acid solutions were added to the saturated mercuric chloride solution and hydrogen sulphide gas was passed through them at a boiling temperature, blackish precipitates produced in the case of 10 N and 1 N were somewhat tinged of red.
 - 17) The blackish sulphides maintained in variously concentrated ammonium hydroxide solutions were enclosed with a drop of the saturated solution of sodium sulphide in the sealed glass-tubes and heated in the air-bath at $95^{\circ} \sim 100^{\circ} \text{C}$. for forty hours but no changes were recognizable on color of the sulphides.
 - 18) When each 10 c.c. of sulphuric acid of various normality was added to the black-colored precipitate obtained by passing hydrogen sulphide gas through 10 c.c. of the saturated mercuric chloride solution at a room temperature, no changes were observable on the very sulphide in each case.
 - 19) When each 10 c.c. of sulphuric acid of various normality was added to the same quantity of the saturated mercuric chloride solution and then hydrogen sulphide gas was passed through the solution thus obtained at a room temperature, the black-colored sulphides were produced.
 - 20) a) When each 10 c.c. of sulphuric acid of various normality was added to the black-colored sulphide and then neutralized with the same quantity of equivalent sodium hydroxide solution, no changes were observable on the precipitate.
b) When each 10 c.c. of sodium hydroxide solution of various normality and then neutralized with the

YOSHIHARU UMEGAKI

- same quantity of equivalent sulphuric acid, the results obtained were similar to those in the case of hydrochloric acid.
- 21) a) Each 10 c.c. of sulphuric acid of various normality and then the same quantity of equivalent sodium hydroxide solution were added to the saturated mercuric chloride solution. When hydrogen sulphide gas was introduced into the solution thus obtained, black-greyish sulphides were deposited in the cases of 10 N and 1 N but blackish precipitates, in other cases.
- b) Each 10 c.c. of sodium hydroxide solution of various normality and then the same quantity of equivalent sulphuric acid were added to the saturated mercuric chloride solution. When hydrogen sulphide gas was passed through the solution thus obtained, the results similar to those in the case of a) were obtained.
- 22) When the sulphides prepared through the process of 21) were boiled with some drops of the saturated solution of sodium sulphide, the color of the precipitate varied into vermilion.
- 23) When hydrogen sulphide gas was passed through the saturated mercuric chloride solution previously mingled with the same quantity of variously concentrated sulphuric acid at a boiling temperature, the blackish sulphide was produced in each case.
- 24) a) When each 10 c.c. of variously concentrated sulphuric acid was added to the solution including the black-colored sulphide deposited by passing hydrogen sulphide gas through the saturated mercuric chloride solution at a boiling temperature, the color of the sulphides remained intact in each case.
- b) When each 10 c.c. of sodium hydroxide solution of various normality was added to the solution maintaining the blackish sulphides deposited through the process same as in the case of a), the color of the precipitates was invariable but the sulphides were dissolved into solution of more than 1 N.
- 25) a) When the solutions obtained through the process of 24) a) were neutralized with the same quantity of equivalent sodium hydroxide solution, no changes were recognizable on the precipitates.
- b) When the solutions obtained through the process of 24) b) were neutralized with the same quantity of equivalent sulphuric acid, the results obtained were similar to those in the case of a).
- 26) a) Each 10 c.c. of sulphuric acid of various normality and then the same quantity of equivalent sodium hydroxide solution were added to the saturated mercuric chloride solution. Blackish sulphides were deposited by passing hydrogen sulphide gas through the solution thus obtained at a room temperature but tinged of brown only in the case of 10 N.
- b) Each 10 c.c. of sodium hydroxide solution of various normality and then the same quantity of equivalent sulphuric acid were added to the saturated mercuric chloride solution. The results obtained were similar to those in the case of a).
- c) No changes were observable merely by boiling the precipitates obtained through the process of a) and b).
- 27) When the blackish sulphides produced through the process of 24) and each drop of the saturated solution of sodium sulphide were enclosed in the sealed glass-tubes and heated in the air-bath at $95^{\circ} \sim 100^{\circ} \text{C.}$ for forty hours, no changes were recognizable on the sulphides.
- 28) When the processes similar to those in the cases of 1) and 2) were repeated with the combination of sulphuric acid and ammonium hydroxide at a room temperature, black-colored sulphides were obtained in all cases.
- 29) If these precipitates were filtered off, washed repeatedly and rinsed into the porcelain crucible maintained on the porcelain triangle, and heated with some drops of the saturated sodium sulphide solution to almost dryness, the central part of them gradually got to bear a red-tinge.
- 30) a) If each 10 c.c. of sulphuric acid containing the black-colored sulphide was neutralized by adding

STUDIES ON QUICKSILVER DEPOSITS

- the same quantity of equivalent ammonium hydroxide solution, the color of the precipitate remained intact in each case.
- b) If each 10 c.c. of ammonium hydroxide solution containing the black-colored sulphide was neutralized by adding the same quantity of equivalent sulphuric acid, the results obtained were similar to those in the case of a).
- 31) a) Each 10 c.c. of sulphuric acid of various normality and then the same quantity of equivalent ammonium hydroxide solution were added to each 10 c.c. of the saturated mercuric chloride solution. When hydrogen sulphide gas was passed through the solution thus obtained at a room temperature, the blackish precipitates were produced in all cases but the addition of a drop of the saturated sodium sulphide solution gave the precipitate obtained in 0.1 N a orange tint.
- b) Each 10 c.c. of ammonium hydroxide solution of various normality and then the same quantity of equivalent sulphuric acid were added to each 10 c.c. of the saturated mercuric chloride solution. When hydrogen sulphide gas was introduced into the solution thus obtained at a room temperature, somewhat brownish sulphides were deposited in the cases of 10 N and 1 N and tinged of red by adding few drops of the saturated sodium sulphide solution.
- 32) The precipitates obtained through the process of 30), even if they were allowed to stand for twenty four hours with few drops of the saturated sodium sulphide solution at a room temperature, remained intact in all cases.
- 33) The precipitates obtained through the process of 31) also gave the results similar to those in the case of 32) through the same process with an exception that the sulphide treated in 0.01 N solution was vermilion-colored.
- 34) a) If the blackish sulphides deposited by passing hydrogen sulphide gas through each 10 c.c. of the saturated mercuric chloride solution at a boiling temperature were mingled with the same quantity of sulphuric acid of various normality, the precipitates were somewhat tinged of brown.
- b) If the blackish sulphides deposited through the process similar to those in the case of a) were mingled with each 10 c.c. of ammonium hydroxide solution of various normality, the very precipitate got to bear a brownish grey tinge in the cases of 10 N and 1 N.
- 35) a) Each 10 c.c. of variously concentrated solution of sulphuric acid was added to the same quantity of the saturated mercuric chloride solution respectively. If hydrogen sulphide gas was passed through these solutions at a boiling temperature, greyish sulphides were deposited in 0.1 N and 0.01 N solutions and blackish ones, in the solutions of other normality.
- b) Each 10 c.c. of ammonium hydroxide solution of various normality was added to the same quantity of the saturated mercuric chloride solution respectively. If hydrogen sulphide gas was passed through these solutions at a boiling temperature, blackish sulphides only were produced.
- 36) a) Each 10 c.c. of variously concentrated solution of sulphuric acid containing the blackish sulphide was neutralized with the same quantity of equivalent ammonium hydroxide solution respectively. If some drops of the saturated sodium sulphide solution were added to these solutions, the very sulphides especially treated in less than 0.1 N solutions were once tinged of orange but regained the black color when they were allowed to stand for some minutes.
- b) Each 10 c.c. of variously concentrated sulphuric acid solution and then the same quantity of equivalent ammonium hydroxide solution were added to each 10 c.c. of the saturated mercuric chloride solution respectively. When hydrogen sulphide gas was passed through these solutions and then some drops of the saturated sodium sulphide solution were added to, the results obtained were similar to those in the case of a).

YOSHIHARU UMEGAKI

- 37) 10 c.c. of 0.1 N sulphuric acid were added to the same quantity of the saturated mercuric chloride solution. When hydrogen sulphide gas was passed through this solution, blackish sulphide was prepared.
- If this unwashed precipitate stored in the porcelain crucible was boiled with some drops of the saturated sodium sulphide solution, no changes were observable on its color.
 - If the very precipitate stored in the porcelain crucible, after washed by decantation, was boiled with three drops of the saturated sodium sulphide solution, no changes were recognizable on its color.
 - If the very precipitate stored in the porcelain crucible, after repeatedly washed, was boiled with five drops of the saturated sodium sulphide solution, it was tinged of yellow.
 - If the very unwashed precipitate stored in the porcelain crucible was boiled with five drops of the saturated sodium sulphide solution, no changes were observed on its color but the solution became turbid.
 - If the very completely washed precipitate stored in the porcelain crucible was boiled with two drops of the saturated sodium sulphide solution; it was partly tinged of brown.
- 38) 10 c.c. of 0.01 N sulphuric acid were added to the same quantity of the saturated mercuric chloride solution. When hydrogen sulphide gas was passed through this solution, black-colored sulphide was deposited. With this precipitate, the procedures similar to those in the case of 37) were repeated.
- No changes were observable on the color of the precipitate.
 - The precipitate was tinged of orange.
 - The precipitate was tinged of brown.
 - The precipitate was tinged of vermilion.
 - The precipitate was tinged of scarlet.
- 39) The solution prepared by adding 10 c.c. of 0.01 N sulphuric acid to the same quantity of the saturated mercuric chloride solution was allowed to stand for twelve hours. When hydrogen sulphide gas was passed through this solution, blackish precipitate was producible but got to bear a vermilion-tint with three drops of the saturated sodium sulphide solution.
- 40) The solution containing the blackish sulphide deposited through the procedures similar to those in the case of 39) was neutralized with equivalent ammoniacal water and boiled for about an hour. When three drops of the saturated sodium sulphide solution were added to this solution, the precipitate thus obtained was tinged partly of brown and partly of vermilion.
- 41) If the solution prepared by adding 10 c.c. of 0.01 N sulphuric acid to the same quantity of the saturated mercuric chloride solution was allowed to stand for three hours, no changes were observable on the color of the precipitate even though the further processes were similar to those in the cases of 39) and 40).
- 42) The black-colored precipitate prepared by introducing hydrogen sulphide gas into the saturated mercuric chloride solution was allowed to stand for twelve hours and then boiled. Even if the saturated sodium sulphide solution was then added to this precipitate, no apparent changes were recognizable.
- 43) a) When 10 c.c. of 0.01 N sulphuric acid was added to the same quantity of the solution containing the blackish sulphide prepared by passing hydrogen sulphide gas through the saturated mercuric chloride solution and the whole solution was then boiled with some drops of the saturated sodium sulphide solution, the very precipitate became tinged of reddish brown.
- b) If the black-colored precipitate obtained through the procedures similar to those in the case of a) was completely washed and then boiled with some drops of the saturated sodium sulphide solution, no changes were observable on its color.
- 44) a) If the blackish sulphide deposited by passing hydrogen sulphide gas through the saturated mercuric chloride solution previously mingled with the same quantity of 0.01 N sulphuric acid was boiled with

STUDIES ON QUICKSILVER DEPOSITS

some drops of the saturated sodium sulphide solution, it was tinged of brown,

- b) If the blackish sulphide prepared through the procedures similar to those in the case of a) was completely washed and then boiled with some drops of the saturated sodium sulphide solution, it was partly tinged of orange.
- 45) a) If the blackish sulphide prepared through the procedures similar to those in the case of 44) at a boiling temperature was boiled with some drops of the saturated sodium sulphide solution, it was partly tinged of orange.
- b) If the very sulphide was completely washed and boiled with some drops of the saturated sodium sulphide solution, it was tinged of vermilion.
- 46) a) If the black-colored sulphide obtained by passing hydrogen sulphide gas through the saturated mercuric chloride solution previously mingled with the same quantity of 0.01 N sulphuric acid was added with ammonium hydroxide solution equivalent to the acid and then boiled with some drops of the saturated sodium sulphide solution, its color remained intact.
- b) If the black-colored sulphide through the processes similar to those in the case of a) was completely washed and boiled with some drops of the saturated sodium sulphide solution, it was partly tinged of vermilion.
- 47) a) If the precipitate produced through the processes similar to those in the case of 46) at a boiling temperature was mingled with ammonium hydroxide solution equivalent to the acid and boiled with some drops of the saturated sodium sulphide solution, no changes were observable on its color.
- b) If the precipitate obtained through the processes similar to those in the case of a) was completely washed and boiled with some drops of the saturated sodium sulphide solution, it was partly tinged of orange.
- 48) 10 c.c. of 0.001 N sulphuric acid were added to the same quantity of the solution containing the black-colored sulphide prepared by passing hydrogen sulphide gas through the saturated mercuric chloride solution. After the whole solution was allowed to stand for about seventy hours, the precipitate only was warmed with various amounts of the saturated sodium sulphide solution on the water-bath.
- a) Blackish but partly reddish tint of the precipitate varied into vermilion with addition of 10 N sodium hydroxide solution.
- b) Vermilion-colored precipitate, partly tinged of brown, turned into brownish one with 10 N ammonium hydroxide solution.
- c) Vermilionish precipitate, partly tinged of black, took a turn for blackish one with 1 N sulphuric acid.
- d) Vermilionish brown-colored precipitate turned into vermilion-tinted one, when it was boiled with 10 N sodium hydroxide solution.
- e) Blackish color of the precipitate varied partly into vermilion with more some drops of sodium sulphide solution.
- f) Brownish precipitate varied its color into vermilion, when it was boiled with 10 N sodium hydroxide solution or more some drops of sodium sulphide solution.
- 49) When hydrogen sulphide gas was introduced into the saturated mercuric chloride solution previously added with the same quantity of 0.01 N sulphuric acid and allowed to stand for about seventy hours, brownish precipitate was produced.
- a) Its color turned into orange merely by adding a drop of the saturated sodium sulphide solution.
- b) The result similar to that in the case of a) was realizable with 10 N sodium hydroxide solution instead of sodium sulphide.
- c) If the very precipitate was enclosed with a drop of the saturated sodium sulphide solution in the

YOSHIHARU UMEGAKI

sealed glass-tube and stored in the air-bath at $95^{\circ}\sim 100^{\circ}$ C. for some minutes, its color took a turn for orange.

d) The result same as that in the case of c) was realizable with 10 N sodium hydroxide solution instead of sodium sulphide.

50) a) When hydrogen sulphide gas was introduced into the saturated mercuric chloride solution previously added with the same quantity of 0.1 N or 0.01 N sulphuric acid, blackish sulphide was produced. When the precipitate was allowed to stand for fifty hours, its color gradually turned into brown at a room temperature.

b) When the very precipitate was warmed at $70^{\circ}\sim 80^{\circ}$ C., similar reaction was completed for about ten hours.

51) a) The black-colored precipitate produced through the procedures similar to those in the case of 50), when it was allowed to stand for three hours, remained its color intact, even if some drops of the saturated sodium sulphide solution were added to at a room temperature.

b) The same precipitate, if it was washed and the acid was thereby completely removed, turned its color into somewhat scarlet by adding some drops of the saturated sodium sulphide solution even at a room temperature.

52) The blackish sulphide prepared through the procedures similar to those mentioned above in variously concentrated sulphuric acid was allowed to stand for forty hours.

a) By adding some drops of the saturated sodium sulphide solution, the very precipitate remained intact in the cases of 10 N and 1 N sulphuric acid but its color gradually took a turn for brown in the case of 0.1 N and for vermilion in the cases of 0.01 N and 0.001 N.

b) When the precipitate was completely washed, its color was black in the case of 10 N, partly red in the case of 1 N and vermilion in the cases of less than 0.1 N simply by adding some drops of the saturated sodium sulphide solution.

53) The blackish sulphide prepared through the procedures similar to those mentioned above especially at a boiling temperature was allowed to stand for forty hours. If some drops of the saturated sodium sulphide solution were added to this precipitate after it was thoroughly washed, remarkable changes were not observable on its color.

54) If the black-colored precipitate produced through the processes same as those in the of 53) was allowed to stand for seventy hours at a room temperature, its color took a turn for vermilion with some drops of the saturated sodium sulphide solution in the cases of less than 0.1 N sulphuric acid.

55) If the same black-colored sulphide was allowed to stand for one hundred hours, its color varied into vermilion in accordance with the quantity of the saturated sodium sulphide solution added.

56) If the black-colored precipitate produced by passing hydrogen sulphide gas through the saturated mercuric chloride solution previously mingled with the same quantity of variously concentrated hydrochloric acid solution was allowed to stand for more than one hundred hours, its color sometimes turned into vermilion in accordance with the quantity of the saturated sodium sulphide solution.

57) When sodium hydroxide solution instead of hydrochloric acid was used at the first step of the above-mentioned procedure, the black color of the precipitate remained intact even if the saturated sodium sulphide solution was added to.

58) Vermilionish precipitate was prepared through the reaction between sodium sulphide solution and the black-colored sulphide deposited by passing hydrogen sulphide gas through the saturated mercuric chloride solution previously added with 0.01 N sulphuric acid.

a) With 10 N and 1 N sulphuric acid, its color was not variable at a room temperature but turned into

STUDIES ON QUICKSILVER DEPOSITS

- scarlet by boiling.
- b) With small quantity of 10 N and 1 N sodium hydroxide solution, its color was not changeable at a room temperature and turned into somewhat scarlet by boiling but regained to vermilion when the system was allowed to cool.
- c) With 12 N hydrochloric acid, the precipitate remained intact at a room temperature but was dissolved when it was boiled. The solution thus obtained was not changeable by adding equivalent sodium hydroxide solution.
- d) The vermilionish color was not changeable by heating at $100^{\circ}\sim 150^{\circ}\text{C}$. in the air-bath. If the very precipitate stored in the porcelain crucible was heated directly on the heater, its color once turned into blackish brown but regained when the precipitate was allowed to cool.
- 59) The blackish color of the precipitate obtained by passing hydrogen sulphide gas through the saturated mercuric chloride solution previously added with the same quantity of 0.01 N hydrochloric acid solution at a room temperature changed into brown when the precipitate was boiled with 1 N sodium hydroxide solution. This was tinged of vermilion with two or three drops of the saturated sodium sulphide solution but regained to black by adding sulphuric acid.
- 60) The black-colored precipitate obtained by passing hydrogen sulphide gas through the saturated mercuric chloride solution previously mingled with the same quantity of 0.01 N sulphuric acid at a room temperature turned its color into brown by boiling with 1 N sodium hydroxide solution. Further changes were quite similar to those in the case of 59).
- 61) The black-colored precipitate prepared by passing hydrogen sulphide gas through the saturated mercuric chloride solution previously mingled with the same quantity of 0.1 N sodium hydroxide solution at a room temperature was tinged of brown when it was allowed to stand for one hundred hours. Further changes were quite similar to those in the case of 59).
- 62) The black-colored precipitate deposited by introducing hydrogen sulphide gas into the saturated mercuric chloride solution at a boiling temperature was allowed to stand for seventy hours. If the very precipitate stored in the porcelain dish was evaporated to almost dryness with some drops of the saturated sodium sulphide solution and again allowed to stand for twenty four hours, its color turned into scarlet but returned to black with considerable amount of 1 N sulphuric acid.
- 63) The black color of the precipitate prepared by passing hydrogen sulphide gas through the saturated mercuric chloride solution previously mingled with the same quantity of 0.01 N sulphuric acid took a turn for brown with some quantity of 1 N sodium hydroxide solution in the course of time. When this precipitate was boiled with some drops of the saturated sodium sulphide solution, its color turned further to vermilion but returned to black by adding diluted sulphuric acid. Even in the same manner, a part of invariable vermilion-color sometimes remained on the precipitate.
- 64) If the brownish precipitate prepared through the processes similar to those in the case of 63) was heated in the evaporating dish directly on the heater, vermilion-color invariable by adding acid was obtained.
- 65) When the blackish precipitate produced through introducing hydrogen sulphide gas into the saturated mercuric chloride solution previously mingled with the same quantity of 0.01 N sulphuric acid was boiled with some c.c. of 1 N sodium hydroxide solution for ten minutes and then with 1 N sulphuric acid, its color turned into brick-red.
- 66) When the blackish sulphide produced through the process similar to that in the case of 65) was warmed with diluted colorless ammonium sulphide solution on the water-bath, its color varied into brown.

- 67) If the procedures similar to those in the cases where the vermilionish sulphides had been prepared by using sodium sulphide solution were repeated with ammonium sulphide, nothing other than brownish precipitates were obtainable.

B The experiments relating to antimony sulphide.

In order to scrutinize whether or not the conditions determined in the synthetic experiments of quick-silver sulphides hold good similarly in those of stibnite or other antimony sulphides, several kinds of procedures believed important for solving the questions under consideration were chosen out of those mentioned in the preceding paragraph.

- 1) The hygroscopic, white powder of antimonous chloride was dissolved in hydrochloric acid, sulphuric acid, nitric acid and sodium hydroxide solution respectively. Merely in the case of ammonium hydroxide, the solution obtained were turbid.
- 2) Reddish orange-colored sulphide deposited by passing hydrogen sulphide gas through the saturated antimonous chloride solution was more easily dissolved into solution than in the case of mercuric sulphide by adding sodium sulphide solution but reprecipitated when sulphuric acid was added to.
- 3) Reddish orange-colored sulphide was obtainable by passing hydrogen sulphide gas through the saturated antimonous chloride solution previously mingled with the same quantity of diluted hydrochloric acid.
- 4) Reddish orange-colored precipitates prepared by passing hydrogen sulphide gas through the saturated antimonous chloride solution previously added with the same quantity of sulphuric acid or hydrochloric acid or sodium hydroxide solution of various normality were warmed on the water-bath for some hours.
 - a) With more addition of variously concentrated sulphuric acid, the precipitates became somewhat tinged of brownish orange.
 - b) If this brownish orange-colored precipitate was boiled with 0.01 N sulphuric acid for more some hours, its color took a turn for lead-grey. When the system was allowed to cool, the precipitate became more and more crystalline but was covered partly with a thin layer of white substance.
 - c) With hydrochloric acid, no changes were observable on the reddish orange-colored precipitate.
 - d) With 10 N and 1 N sodium hydroxide solution, the precipitates were dissolved into solution but, in the cases of other normality, no changes were recognizable on the precipitate.
- 5) It was difficult to prepare the lead-greyish precipitate when the reddish orange-colored sulphide deposited simply by passing hydrogen sulphide gas through the saturated antimonous chloride solution was boiled with 0.01 N sulphuric acid.
- 6) When reddish orange precipitate obtained by passing hydrogen sulphide gas through the saturated antimonous chloride solution previously mingled with 0.01 N sulphuric acid was evaporated to almost dryness with some drops of the saturated sodium sulphide solution on the water-bath, its color was tinged of lead-grey.
- 7) If the lead-greyish precipitate obtained through the procedures similar to those in the case of 4)b) was boiled with certain reagents:
 - a) With more than 1 N solution of sulphuric acid, the solution became turbid.
 - b) With 10 N sodium hydroxide solution, its color returned to yellow and the solution became turbid.
 - c) With 10 N hydrochloric acid, the precipitate was completely dissolved into solution and, in the cases of less than 1 N, the solution was turbid.
 - d) With one-half concentration of the saturated sodium sulphide solution, whitish colloidal solution was obtained and, in the cases of more diluted solution, a part of the precipitate was tinged of orange.

STUDIES ON QUICKSILVER DEPOSITS

C The experiments relating to arsenic sulphide.

In the light of the preceding procedures, the experiments in question were confined to considerable extent.

- 1) When hydrogen sulphide gas was introduced into the saturated arsenous chloride solution, yellowish precipitate was obtained.
- 2) a) When hydrogen sulphide gas was passed through the transparent solution prepared by adding 1 N hydrochloric acid to the white powder of arsenous oxide and then boiling with 0.01 N sulphuric acid for some minutes, yellowish crystalline precipitate was produced.
b) When the very precipitate was allowed to stand overnight and then boiled with some drops of the saturated sodium sulphide solution, its color was partly tinged of cockscomb-red. With more drops of sodium sulphide solution, it became dark-red.
c) By warming the yellowish precipitate prepared through the above-mentioned process on the water-bath with repeated addition of the saturated sodium sulphide solution, its color became more and more reddish.
d) If the reddish precipitate obtained through the preceding process was warmed on the water-bath with 0.01 N sulphuric acid in the test-tube attached with Liebig condenser for two or three weeks, its color gradually returned to yellow.
- 3) When hydrogen sulphide gas was passed through the saturated arsenous oxide solution previously mingled with the same quantity of 0.01 N sulphuric acid and boiled for some minutes, yellowish crystalline precipitate was produced. When this precipitate was treated through the procedures shown in 2), similar results were obtained.
- 4) Even if the yellowish precipitate prepared through the preceding processes was boiled with 0.01 N sulphuric acid for three weeks, no changes were observable on its color.
- 5) When hydrogen sulphide gas was passed through the yellowish solution prepared by dissolving realgar with hydrochloric acid or sulphuric acid, yellowish sulphide was accountably producible.

3. Solubility of the synthesized sulphides.

For convenience, the solubility is here meant by the dissolved amounts of the sulphides under consideration in certain kinds of acid, alkali and salt. It is of course that the reactions with acid or with alkali must essentially be distinguishable one from the other since the former case is concerned in the change of dispersion degree and the latter in the formation of complex salt. Necessary is not the solubility in a true sense but comparison of the apparent solubility for the purpose of this investigation because it seems most significant that more or less amounts of the components in question were brought from the depth, no matter in what state they might have been.

The sulphides prepared for the experiments were completely dried up in the air-bath at 95°~100°C. and allowed to cool in the desiccator. 0.3~0.5 gr. of them were accurately weighed out into the test-tube and digested with each 10 c.c. of the reagents. In order to keep the concentration and amount of the con-

YOSHIHARU UMEGAKI

tents constant, the test-tube was connected with Liebig condenser and warmed in boiling water for two hours. One of the reasons why the experiments were carried out at a boiling temperature is based on the presumption that low temperature hydrothermal minerals such as cinnabar, stibnite, realgar etc. should have been deposited in the condition not far from this temperature. After two hours' duration, the precipitate contained in the solution was filtered by means of Gooch crucible previously weighed and washed thoroughly with acid, if need be. The crucible maintaining the residue was dried up in the air-bath at $95^{\circ}\sim 100^{\circ}\text{C}$. and weighed after it was allowed to cool in the desiccator. The solubility of the sulphides in 10 c.c. of any reagents was thus estimated by the decrease of its amount. The data obtained, though they may represent nothing but the relative values of solubility in special case, are tabulated as follows:

STUDIES ON QUICKSILVER DEPOSITS

Table 1 a

(The data for black-colored mercuric sulphide prepared by passing hydrogen sulphide gas through the acidified solution of mercuric chloride at a room temperature)

Reagent used for the experiment	Normality of reagent	Residual amount in wt. %
Hydrochloric acid	1	90.49
	0.1	94.02
	0.01	95.62
Sulphuric acid	1	82.42
	0.1	84.72
	0.01	98.54
Sodium hydroxide	1	83.00
	0.1	92.15
	0.01	95.77
Ammonium hydroxide	1	92.50
	0.1	96.00
	0.01	98.57
Sodium sulphide	1/2	6.85
	1/4	46.46
	1/8	82.95
	1/16	88.84
Sodium carbonate	1	87.20
	0.1	91.73
	0.01	95.59

Table 1 b

(The data for vermilion-colored mercuric sulphide prepared through the process shown in the synthetic experiment 55))

Reagent used for the experiment	Normality of reagent	Residual amount in wt. %
Hydrochloric acid	1	97.96
	0.1	98.32
	0.01	98.69
Sulphuric acid	1	96.99
	0.1	98.06
	0.01	98.33
Sodium hydroxide	1	92.89
	0.1	97.00
	0.01	98.73
Ammonium hydroxide	1	96.48
	0.1	97.50
	0.01	98.90
Sodium sulphide	1/2	47.43
	1/4	68.29
	1/8	85.91
	1/16	89.87
Sodium carbonate	1	96.55
	0.1	98.00
	0.01	99.32

YOSHIHARU UMEGAKI

Table 1. c

(The data for scarlet-colored mercuric sulphide prepared through the process shown in the synthetic experiment 38) e))

Reagent used for the experiment	Normality of reagent	Residual amount in wt. %
Hydrochloric acid	1	96.16
	0.1	97.27
	0.01	98.92
Sulphuric acid	1	91.88
	0.1	95.41
	0.01	98.99
Sodium hydroxide	1	89.25
	0.1	94.98
	0.01	98.21
Ammonium hydroxide	1	92.95
	0.1	95.89
	0.01	98.84
Sodium sulphide	1/2	9.75
	1/4	75.43
	1/8	87.76
	1/16	90.00
Sodium carbonate	1	92.92
	0.1	95.88
	0.01	97.01

Table 1. d

(The data for cinnabar from Kambe Mine, Nara Pref.)

Reagent used for the experiment	Normality of reagent	Residual amount in wt. %
Hydrochloric acid	1	79.04
	0.1	82.88
	0.01	96.37
Sulphuric acid	1	82.01
	0.1	92.48
	0.01	97.80
Sodium hydroxide	1	86.20
	0.1	95.84
	0.01	98.62
Ammonium hydroxide	1	85.83
	0.1	95.67
	0.01	99.44
Sodium sulphide	1/2	54.62
	1/4	70.35
	1/8	81.74
	1/16	88.39
Sodium carbonate	1	92.88
	0.1	95.70
	0.01	97.26

STUDIES ON QUICKSILVER DEPOSITS

Table 2 a

(The data for lead-greyish antimonous sulphide prepared through the process shown in the synthetic experiment 4) b))

Reagent used for the experiment	Normality of reagent	Residual amount in wt. %
Hydrochloric acid	1	86.76
	0.1	96.32
	0.01	97.58
Sulphuric acid	1	95.90
	0.1	96.24
	0.01	97.15
Sodium hydroxide	1	74.67
	0.1	87.71
	0.01	95.29
Ammonium hydroxide	1	85.19
	0.1	89.00
	0.01	95.19
Sodium sulphide	1/2	2.61
	1/4	83.17
	1/8	90.08
	1/16	92.90
Sodium carbonate	1	86.74
	0.1	91.05
	0.01	94.39

Table 2. b

(The data for stibnite from Kano Mine, Yamaguchi Pref.)

Reagent used for the experiment	Normality of reagent	Residual amount in wt. %
Hydrochloric acid	1	97.63
	0.1	98.95
	0.01	99.19
Sulphuric acid	1	97.99
	0.1	98.91
	0.01	99.90
Sodium hydroxide	1	44.31
	0.1	85.29
	0.01	93.81
Ammonium hydroxide	1	95.69
	0.1	98.02
	0.01	99.77
Sodium sulphide	1/2	34.74
	1/4	49.17
	1/8	75.37
	1/16	88.33
Sodium carbonate	1	96.82
	0.1	97.06
	0.01	98.27

YOSHIHARU UMEGAKI

Table 3 a

(The data for yellowish arsenious sulphide prepared through the process shown in the synthetic experiment 3)

Reagent used for the experiment	Normality of reagent	Residual amount in wt. %
Hydrochloric acid	1	95.61
	0.1	96.09
	0.01	97.18
Sulphuric acid	1	94.95
	0.1	96.01
	0.01	97.21
Sodium hydroxide	1	4.18
	0.1	46.77
	0.01	82.47
Ammonium hydroxide	1	10.00
	0.1	49.49
	0.01	85.78
Sodium sulphide	1/2	7.93
	1/4	39.57
	1/8	60.15
	1/16	85.99
Sodium carbonate	1	74.19
	0.1	80.95
	0.01	92.23

Table 3 b

(The data for realgar from Nyu Mine, Mie Pref.)

Reagent used for the experiment	Normality of reagent	Residual amount in wt. %
Hydrochloric acid	1	89.89
	0.1	92.40
	0.01	94.50
Sulphuric acid	1	90.86
	0.1	95.66
	0.01	96.82
Sodium hydroxide	1	82.07
	0.1	93.06
	0.01	97.98
Ammonium hydroxide	1	95.22
	0.1	99.62
	0.01	100.00
Sodium sulphide	1/2	71.77
	1/4	79.56
	1/8	87.98
	1/16	90.00
Sodium carbonate	1	92.08
	0.1	94.31
	0.01	95.23

STUDIES ON QUICKSILVER DEPOSITS

In the column of normality of sodium sulphide, 1/2, 1/4,.....represent one-half, one-fourth,..... concentration of the saturated solution respectively. The experiments with nitric acid were intentionally excluded because this very acid, as was shown in the preliminary test in part I, often reacts as an oxidizing agent and its use is apt to confuse the results.

4. Volatilizability of the synthesized sulphides.

With all the previous data as to the subliming point of some sulphide minerals such as cinnabar, stibnite, realgar etc., the volatilizable amounts of the synthesized sulphides were weighed in order to examine their stability for the elevation of temperature.

0.2~0.3 gr. of the sulphides stored in the porcelain crucibles were heated on the water-bath, in the air-bath and directly on the heater at the definite temperature and then the apparent decrease of their weight was regarded as the amount of volatilization.

The results obtained are shown in the following tables wherein the amounts volatilized are indicated by the percentage referring to the weight taken as the sample.

Table 4

(The data for black-colored mercuric sulphide prepared through the process shown in the synthetic experiment 7)

Condition	Duration in hours	Volatilized amount in wt. %
Heated on the water-bath at 96°~98° C.	2	0.00
	4	0.00
	10	0.00
Heated in the air-bath at 120° C.	2	0.00
	4	0.00
Heated directly on the heater at ca. 200° C.	1	13.14
	2(1)	24.59
	2(2)	24.80
	4	46.23
	6	65.23
Heated on the heater at ca. 250° C.	0.5	15.08
	1	29.33
Heated on the heater at ca. 300° C.	1	100.00
Heated with active carbon on the water-bath at 96°~98° C.	2	11.03
	4	17.82
	6	23.15
Heated with active carbon on the heater at ca. 200° C.	2	37.03

Table 5

(The data for lead-greyish antimonous sulphide prepared through the process shown in the synthetic experiment 4) b))

Condition	Duration in hours	Volatilized amount in wt. %
Heated on the heater at ca. 150° C.	2(1)	0.31
	2(2)	0.26
Heated on the heater at ca. 200° C.	2(1)	0.37
	2(2)	0.28

When heated at ca. 250° C., the color of the sulphide varied into white probably owing to the oxidation.

No experiments as to the arsenic sulphides were carried out but the volatilized amount of arsenic chloride was estimated at 1.35% in weight at 96°~98° C. after two hours' duration.

5. Specific gravity of the synthesized sulphides.

As far as the substances composed of mutually similar chemical constituents are concerned, the identity of their specific gravity has to suggest the resemblance of the inner structure to certain extent. On the basis of this presumption, these measurements were put in practice as a nimble means of considering the results of the synthetic experiments, while it also is evident that the values of density have a intimate connection with the numbers of atoms or ions included in an unit-cell.

The data shown hereunder were obtained through a ordinary pycnometer method at a room temperature and concerned merely in some representative sulphides.

(a) Black-colored mercuric sulphide deposited through the process shown in the synthetic experiment 7)	7.50~7.90
(b) Black-colored mercuric sulphide deposited through the process shown in the synthetic experiment 19)	7.48~7.78
(c) Brown-colored mercuric sulphide deposited through the process shown in the synthetic experiment 50)	8.02~8.12
(d) Vermilion-colored mercuric sulphide deposited through the process shown in the synthetic experiment 55)	8.05~8.17
(e) Scarlet-colored mercuric sulphide deposited through the process shown in the synthetic experiment 58) a)	8.07~8.15
(f) Lead-greyish antimonous sulphide deposited through the process shown in the synthetic experiment 4) b)	4.30~4.58
(g) Yellow-colored arsenous sulphide deposited through the process shown in the synthetic experiment 3)	3.35~3.58
(h) Red-colored arsenous sulphide deposited through the process shown in the synthetic experiment 2) b)	3.41~3.51

STUDIES ON QUICKSILVER DEPOSITS

The results of quantitative chemical analysis show that no traces of alkali metals were included in the sulphides (d) and (e) but few in (h):

6. X-ray analysis of the synthesized sulphides.

To give the decisive answer to the question whether or not the inner architectures of the sulphides under consideration are consistent with those of low temperature hydrothermal sulphide minerals such as cinnabar, stibnite and so on, the x-ray diffraction patterns obtained by means of the powder method using Cu K_{α} (slightly including K_{β}) -radiation were scrutinized. Both of the cylindrical and flat films were used in these experiments, for it is sure that, although the use of the former is more desirable for complete analysis of the crystal structure, the latter also can serve if the purpose is simply to compare the inner structure of synthesized specimen with the one shown by native minerals.

The data obtained are related specifically to some representative sulphides believed most important to reach the main object. The calculated spacings are given in the following tables, wherein the unit is represented in Å and the symbols such as s, m and w indicate the relative intensity of the diffracted x-ray: That is to say, s means strong, m medial and w weak, respectively.

Table 6 a

(The data for mercuric sulphides)

(a)		(b)		(c)		(d)	
3.89	w	3.90	w	9.01	w	3.88	w
3.69	w	3.69	w	4.48	w	3.37	s
3.35	s	3.35	s	3.91	w	2.93	w
3.17	m	3.16	m	3.37	s	2.26	w
2.85	s	2.85	s	2.93	w	2.06	m
2.36	w	2.35	w	2.58	w	1.93	w
2.29	w	2.29	w	2.23	w	1.76	m
2.06	m	2.06	m	2.06	m	1.68	w
2.01	w	2.01	w	1.93	w	1.46	w
1.97	m	1.97	m	1.76	m	1.33	w
1.90	w	1.90	w	1.69	w	1.30	w
1.76	w	1.76	w				
1.73	m	1.72	m				
1.67	m	1.66	m				
1.57	w	1.56	w				
1.43	w	1.43	w				
1.40	w	1.39	w				
1.34	w	1.34	w				
1.30	w	1.30	w				
1.25	w	1.25	w				
1.18	w	1.18	w				

YOSHIHARU UMEGAKI

- (a) Cinnabar from Kambe Mine, Nara Pref. (See Plates 53 and 57)
- (b) Brown-colored mercuric sulphide prepared through the synthetic experiment 50). (See Plates 54 and 58)
- (c) Black-colored mercuric sulphide prepared through the synthetic experiment 23). (See Plates 55 and 60)
- (d) Black-colored mercuric sulphide prepared through the synthetic experiment 19). (See Plates 59 and 61)

It must here be noticed that the diffraction patterns of vermilion and scarlet-tinged modifications of mercuric sulphides synthetically obtained also are consistent perfectly with those of (a) and (b). Moreover, the blackish mercuric sulphide deposited through a ordinary method shows the pattern quite same as the one given in the case of (d)

Considering both Hull's chart and the theoretical values calculated from the spacings cited in the above-mentioned table, it results that cinnabar (a) and brownish sulphide (b) as well as other similar modifications are to have the rhombohedral lattice of hexagonal system where a is 4.11 Å and c is 9.46 Å, the specimen (c) belongs to the face-centered tetragonal lattice where a is 4.48 Å and c is 5.16 Å and (d) to the face-centered cubic lattice where a is 5.83 Å.

Table 6 b

(The data for antimony sulphide)

(a)		(b)		(c)	
4.67	w	6.22	w	6.26	w
3.99	w	4.99	w	5.00	m
3.50	m	4.04	w	3.97	w
3.15	s	3.62	m	3.53	s
2.69	m	3.43	s	3.05	s
2.48	w	3.08	s	2.73	s
2.27	w	2.78	m	2.66	m
2.06	w	2.54	m	2.54	m
1.95	m	2.38	w	2.43	w
1.81	w	2.25	w	2.22	w
1.72	w	2.18	w	2.09	m
1.66	m	2.05	w	1.90	s
		1.95	m	1.72	w
		1.88	w	1.68	m
		1.82	w	1.63	w
		1.70	w		
		1.66	m		

- (a) Stibnite from Kano Mine, Yamaguchi Pref. (See Plate 62)
- (b) Lead-greyish antimonous sulphide prepared through the synthetic experiment 4) b). (See plates 63 and 64)
- (c) Brownish orange-colored antimonous sulphide prepared through the synthetic experiment 4) a). (See plate 65)

STUDIES ON QUICKSILVER DEPOSITS

Since the data shown in the preceding table were obtained simply from the diffraction patterns on the flat films, there may be some obscurity in the parts distant from the undeviated center but the results are that stibnite (a) belongs to the orthorhombic lattice where a is 9.45 Å, b 11.19 Å and c 3.90 Å, lead-greyish sulphide (b) to a similar lattice where a is 9.24 Å, b 11.62 Å and c 3.90 Å and brownish orange-colored one (c) to the face-centered tetragonal lattice where a is 5.00 Å and c is 6.66 Å ; while orange-reddish modification prepared through a usual method at a room temperature is amorphous. (See Plate 66). It is to be noted that the values shown in the column of (c) are almost completely identical with those given for stibnite by T. Kubo.⁽⁴⁰⁾ An inspection of the diffraction patterns indicates that both native and lead-greyish sulphide have a resemblance in the tendency and intensity of x-ray diffraction although they are different actually in the calculated values of lattice constants. If the impurities, for instance, antimony oxychloride or any other oxy-compounds included in the synthesized sulphides are wiped away or reaction-time is properly prolonged, far more conformity may be realized in their crystal structures. Most important is that the possibility for lead-greyish modification similar to native stibnite to be produced was ascertained similarly in the case of the relation of the synthesized mercuric sulphides to cinnabar.

Table 6 c

(The data for arsenic sulphides)

(a)	(b)	(c)	(d)
4.33 w	4.90 m	5.90 w	6.58 m
3.41 s	4.18 m	4.91 w	5.76 w
3.25 w	3.80 w	4.18 m	4.04 w
3.00 s	3.23 w	3.79 w	3.58 w
2.08 w	3.03 m (broad)	3.23 m	3.23 s
2.00 w	2.48 w	2.84 s	2.78 s
1.72 w	2.34 w	2.55 w	2.53 s
1.65 w		2.34 w	2.26 w
		2.13 w	2.16 w
		2.05 w	1.96 w
		1.93 w	1.86 w
		1.75 w	1.66 m
		1.69 m	1.59 w
			1.54 w

(a) Realgar from Nyu Mine, Mie Pref.

(See plate 67)

(b) Cockscomb-colored arsenous sulphide prepared through the synthetic experiment 2) b).

(See plate 68)

(c) Vermilion-colored arsenous sulphide prepared through the synthetic experiment 2) c).

(See plate 69)

(d) Yellowish arsenic sulphide prepared through
the synthetic experiment 2) a) or 3).

(See plates 70 and 71)

If the lattice constants are once roughly estimated from Dana's values concerning the axial ratio and axial angle and then calculated on the basis of the data really obtained from the diffraction patterns, it results that realgar (a) shows a monoclinic lattice where a is 7.65 Å, b 5.52 Å and c 5.31 Å, the modification (c) a simple tetragonal lattice where a is 5.91 Å and c is 3.79 Å and (d), if it is considered to be identical with orpiment, a monoclinic lattice, the axial angle of which is approximately rectangular, or rather orthorhombic lattice where a is 5.71 Å, b 9.79 Å and c 6.68 Å: while the structure of the modification (b), however, cannot be determined simply from these incomplete data. Further allusion to the particular behavior of arsenic sulphides seems necessary, because it happens that amorphous modification also is producible at a certain stage in the synthetic process even though it is evidently crystalline in the beginning. Since these results, however, were obtained in the cases of three or four hours' duration of exposure for x-ray radiation, any other patterns might have been revealed with more prolongation of time.

7. Variation of PH-values in the media concerned.

As a supplementary means of determining the state of the solution in question and finding a clue to interpreting the process of transition of the black-colored mercuric sulphide to the reddish modification, the variation of potential difference relating to the hydrogen-ion concentration in certain media, where the precipitate was produced, was measured continuously in the course of time. Procedures and apparatus used for the experiments were as follows:

30 c.c. of the solution maintaining the blackish sulphide prepared by saturating hydrogen sulphide gas in the saturated mercuric chloride solution previously mingled with the same quantity of 0.01 N sulphuric acid were kept in a glass-bottle corked with a gum-stopper, through which both a carbon-electrode and a U-shaped glass-tube filled with agar-agar dissolving the saturated solution of potassium chloride were immersed in the solution concerned. The carbon-rods provided for electrode were selected out of those used for spectroscopic analysis and carefully purified by means of boiling in aqua regia for several days and then washing thoroughly. In order to fill their probable cavities and thereby to keep the effect of absorption of hydrogen sulphide gas existing in the system constant, they were boiled in the molten paraffin at ca. 150° C. for about twenty minutes and allowed to cool at a room temperature, and one sides of them were polished away to soak directly in the solution. It

STUDIES ON QUICKSILVER DEPOSITS

was a reason of why Pt- (H^+) electrode and other metallic ones were not used for these experiments that the definite values of potential difference were hardly obtainable on account of their reaction with hydrogen sulphide. Since the surface of the carbon-electrode soaked in the solution was, in this case, saturated with hydrogen sulphide gas, it was to play a role as a special sort of carbon-hydrogen sulphide gas electrode in the system under consideration. Potential difference between the saturated calomel-electrode and the carbon-electrode thus obtained was measured by a compensation method using a mirror-galvanometer. Prior to each experiment, the purity of the carbon-electrode was examined and standardized by the reading referring to its potential difference in pure water for the calomel-electrode connected with a liquid-junction of potassium chloride alluded to already.

(a) The data for the potential difference between the calomel-electrode and the carbon-electrode immersed in pure water and pure sulphuric acid of various normality are shown in Fig. 17 where pH-values were derived from the relation of ionization degree to the actual normality of the acid.

(b) The data concerning the potential difference or pH-values in variously concentrated sulphuric acid saturated with hydrogen sulphide gas are shown in Fig. 18, wherefrom the relations of the reading of potential difference in volts, pH-values and the normality of the acid are deducible.

(c) The blackish mercuric sulphide was prepared by saturating hydrogen sulphide gas in the saturated mercuric chloride solution previously mingled with the same quantity of sulphuric acid. As soon as the solution was saturated with hydrogen sulphide and the precipitation was completed, the system was perfectly closed and the potential difference appeared with variation of conditions in the system concerned was continuously read.

The data in the case where the system was treated with 0.01 N sulphuric acid are given in Fig. 19 where the symbol \times represents the changes of the state at 12° - 16° C., \circ those at 14° - 18° C. and \bullet those at 40° C., respectively.

The data in the case of the acid of other normality are shown in Fig. 20 where the symbol \circ indicates the changes of the state in the media treated with 0.1 N sulphuric acid at 12° - 16° C. and \bullet those in the case of 0.001 N.

The variations of potential difference or, consequently, the correspondent pH-values in variously concentrated sulphuric acid containing the black-colored mercuric sulphide and saturated with hydrogen sulphide were diagrammatically shown in these figures, wherein a rapid decrease of the reading was appeared when particles of the blackish modification began to take a turn for brownish one quite similar to cinnabar in the inner architecture.

The results thus obtained surely indicate that :

- (1) The reading for pH decreases from the definite values in the beginning

- to somewhat less than 3 but the state of media in question is still acidic;
- (2) Duration-time necessary for transition from one to the other is shorter in the solution treated with 0.01 N sulphuric acid than in the case of other normality;
- (3) In the solution treated with 0.1 N sulphuric acid, the reading was almost invariable at a room temperature lower than 16° C. even for a month but was not always so at a higher temperature. At ca. 30° C., for instance, the fact was that the transition was nearly completed for about three weeks, though the variation of pH-values was not accurately read.
- (4) It, of course, was a general rule that, the higher was the temperature, the sooner the transition was completed but it is not necessary to consider such a higher temperature as has hitherto been assumed.
- (5) Deviation of the reading in the beginning from normal one seems to be ascribable to more or less amount of absorption of hydrogen sulphide on the surface of the carbon-electrode.
- (6) When 0.01 N sulphuric acid was added to the same quantity of the saturated mercuric chloride solution and then hydrogen sulphide gas was therein saturated, the resultant concentration of hydrogen-ion in the system is, as can easily be calculated, considered to have been distant not much far from 0.01 N because the acidity derived mainly from the reaction between mercuric chloride and hydrogen sulphide also must be taken into account.
- (7) The measurement at a temperature higher than the melting point of paraffin was impossible with the electrode applied in these experiments, so that no data concerning another blackish modification of mercuric sulphide prepared at a boiling temperature were obtainable.

(3) Scrutiny of the experimental data.

Variouly colored mercuric sulphides showing the crystal structures completely identical with that of cinnabar are preparable through plentiful kinds of synthetic manipulations, among which it appears most helpful that the blackish mercuric sulphide deposited by passing hydrogen sulphide gas through the mercuric salt solution, no matter to what kind it may belong, is allowed to stand in ca. 0.01 N sulphuric acid for a long while or is simply boiled in sulphuric acid after few drops of sodium sulphide solution or of sodium hydroxide solution are added. More important conclusion derived from the experiments is that the condition necessary for preparing the sulphides in question is not the presence of alkali component but that of acid and of sulphide-ion in the media concerned, because, for instance, brown-colored mercuric sulphide quite same as cinnabar in its inner structure is easily obtainable with

STUDIES ON QUICKSILVER DEPOSITS

no traces of alkalis. It is desirable that hydrogen sulphide, even in traces, takes part in the reaction, since it seems difficult to produce the "artificial cinnabar" even in properly diluted sulphuric acid if hydrogen sulphide be previously expelled out from the system in question. When sodium hydroxide is added to the solution containing hydrogen sulphide, sodium sulphide is accountably producible. The effects thus obtained become similar to those in the case where the very sulphide of its own plays a role in the reaction. Be that as it may, the existence of sodium sulphide, though it surely is helpful for changing the color of mercuric sulphides from black to vermilion or scarlet, has not much significance specifically in the variation of their inner structure to that of cinnabar, as the results of quantitative chemical analysis indicate no traces of alkali components in vermilion- or scarlet-tinted sulphides and the configuration of unit-cell is surely variable without sodium sulphide. With all the preceding view, as was frequently alluded to, that alkali sulphide can precipitate cinnabar in alkaline state,¹⁷ the very sulphide only can, but for any other preparative procedures, never deposit the modification similar to cinnabar and, furthermore, hardly dissolve the mercuric sulphides or others when it is sufficiently diluted to the same extent as in the case of acid. It consequently seems that a role of sodium sulphide in these reactions is nothing but a sort of catalyzer for merely changing the color of mercuric sulphides. On the other hand, the use of ammonium sulphide instead of sodium sulphide results in the deposition of brownish modification, though the objective is thereby similarly achievable.

It was experimentally proved that ca. 0.01 N sulphuric acid gives the most remarkable influence on the variation of lattice constants but it is not always difficult to realize the similar effect by means of hydrochloric acid. Nitric acid only must be excluded on account of its strength of oxydizing power. At any rate, even granting that the well-known law, proposed and modified by some authors such as Clausius, Mosotti, Debye and so on, as to the intimate connection of molecular polarizability to dielectric constant of media or the concentration of hydrogen-ion in this case may give a clue to interpreting the mechanism of variability of the crystal structures to certain extent, much more stress of investigation must be laid on the kind of acid taking part in the reaction, the behavior of hydrogen sulphide or sulphide-ion and the duration of reaction-time. Although it is, only from these experiments, still now a pending question why variously colored mercuric sulphides become to be conformable with cinnabar in their inner architectures, it may be presumed that these modifications also are destined to change their apparent color to scarlet or brick-red with the extreme prolongation of immersion-time in such media as was referred to already. As to these subjects, the writer, hence, cannot agree

easily with the simple opinion proposed by Dreyer⁽²⁷⁾ who ascribed the tinge of cinnabar merely to the impurities included.

As regards the blackish variety, the sulphide deposited in acidic state at a lower temperature has been simply believed as metacinnabarite but it is, as a matter of fact, questionable which modifications are most close to the very mineral, for many kinds (at least two in these experiments) of blackish sulphides can be prepared in certain conditions. As the case may be, some of them are obtainable even at a temperature higher than for such modification as is completely identical with cinnabar. Consequently, it seems very risky to identify the mineral macroscopically or even with the help of a microscope especially in this case and it also is necessary to emphasize that the essential differences among minerals cannot be determined simply according to their apparent color or textures under microscope.

On the other hand, such paragenetic relations of cinnabar to other modifications as are expected from the experiments are actually observable in some sections if carefully inspected. (See Photo-plates 45-51) In the section of ore from Saeki Mine, gradual variation of metacinnabarite to cinnabar evidently shows the coincidence with the results obtained in the synthetic experiments wherein the blackish sulphide once deposited probably through the reaction of hydrogen sulphide with certain mercuric salt solutions, no matter to what kind they may belong, varies first into another modification and then into cinnabar. In another section of the specimen obtained from a place near Shiomoto Shrine in Oita Pref., ordinary kind of cinnabar is co-existent with brownish grey-colored sulphide which, at a glance, may be mistaken as metacinnabarite even under a microscope but is essentially cinnabar itself probably similar to the brownish variety synthetically obtained.

As a result of inspection of the experimental evidences obtained above, the writer cannot help taking up the subject relating to transition appeared among various modifications of a substance. It is usually believed that transition, in a common-sense, takes place merely with the variation of temperature but, as is easily comprehended from the preceding synthetic processes, the considerations must be referred not only to the temperature but also to the conditions of then-existing media, the duration of time and predicatively the co-existence of impurities; because, for instance, blackish mercuric sulphide can be changed into brownish one identical with cinnabar in acidic state even at a room temperature for scores of hours. Previous data connecting with transition-point measured in a dry state without considerations on the factors mentioned above, therefore, have nothing but a physico-chemical meaning but can not clarify the phenomena of transition among native minerals in a true sense. Standing at this point of view, it follows that the transition-temperature, if it was

STUDIES ON QUICKSILVER DEPOSITS

determined simply in a 'dry' state, may be scarcely significant as a so-called geologic thermometer.

Another noticeable fact is that the conditions suitable for the synthesis of cinnabar hold, just as they are, good in the case of precipitation of artificial stibnite from antimony sulphides obtained through a usual procedure. The lattice constants of the synthesized stibnite are somewhat deviated from those of the native mineral but such a difference as was shown on the diffraction pattern may be permissible especially when slight amounts of impurities (presumably oxy-compounds in this case) are contained. It is clear that the modification similar to the native stibnite is preparable in a boiling state in the course of time shorter than for mercuric sulphide. More precisely speaking, orange-colored amorphous sulphide produced through a ordinary method changes its color through brownish orange (corresponding to metastibnite) and to lead-grey (identical with stibnite). Also in this case, the transition-temperature is obscure since both metastibnite and stibnite are similarly producible in a boiling state but there may be a slight difference between them only in such regard that the latter is prepared in a longer duration of time than for the former. Inasmuch as it seems, at present, nearly impossible to obtain the modification conformable with stibnite at a room temperature, it is naturally presumable that native stibnite also is deposited at a temperature somewhat higher than for cinnabar. This coincides evidently with the results attained from the field observation.

As to the arsenic sulphides, yellowish crystalline variety anticipated from its color as corresponding to orpiment is deposited at a room temperature through the same processes as were attempted for other kinds of sulphides but it is still now pending whether or not the reddish arsenous sulphide identical with realgar may be producible through those manipulations, although another kind of reddish one is proven as obtainable in the experiment. Remarkable is that these sulphides indicate a special tendency: There yields sometimes a intermediate amorphous phase between yellowish and reddish one if the transition of amorphous modification to crystalline one or vice versa be considered as a normal transition. It results that four or five kinds of modifications are counted in the case of arsenic sulphides.

Now, with regard to the experimental data connecting with the solubility of synthesized sulphides in certain reagents, some allusion seems necessary. To the question in what kind of process the elements such as mercury, antimony and arsenic have been extracted out from the depth, it is difficult or impossible to give an explicit answer. Though the formation of complex salt by adding alkali sulphide to any given metal sulphides in alkaline state may be convenient for dissolving them, it seems unreasonable to expect such a high concentra-

tion as can dissolve them in native solution. On the basis of these considerations, the experiments concerning the solubility have been carried out. As a result, it becomes clear that: (a) The dissolved amounts of sulphides in question correspond to the normality of reagents; (b) As far as the reagents show comparatively higher normality, sodium sulphide is, of course, the most effective solvent above all and then sodium hydroxide follows; (c) As the reagents are diluted, the difference of the dissolved amounts more and more decreases and, even in ca. 1/20 N, though such a high concentration can by no means be presumed in native solution at a later stage of mineralization process, it is not much more than few percents. Since the experiments have been practised in a boiling state, the dissolved quantity of sulphides may be different from those attained at a ordinary temperature but the difference among the dissolved amounts can, simply according to whether then-reacting agents may be alkali or acid, be scarcely recognized in extremely diluted solutions. This is noticeable as a disproof for the opinion supporting merely the hypothesis of complex salt.

As far as the specific gravity is concerned, the results obtained are that, in the case of mercuric sulphides, the nearer its value approaches to that of cinnabar, the more resemblance to the very mineral is attainable in the inner architecture, as to which the analysis was achieved from the data of x-ray diffraction and, in other sulphides, there seems to be no remarkable deviations between the values shown by either native minerals or the synthesized sulphides.

In spite of miscellaneous kinds of sulphides prepared through various processes, the data relating to x-ray analysis may be too few to interpret them all. Specifically in the case of mercuric sulphides, it is surely believed that more kinds of modifications other than those already identified and expected should be discovered by complete analysis of all specimens but the writer particularly desired to compare the inner structure of cinnabar with those of artificial sulphides produced in certain conditions and to find the coincidence among them rather than to accomplish the analysis of x-ray diffraction patterns. Judging from this point of view, the data obtained evidently gives the necessary and sufficient answer to the subject under consideration. An inspection of them indicates that: (a) One of the mercuric sulphides synthesized in acidic media is identical with cinnabar and two other modifications are at the same time obtainable; (b) One of the antimony sulphides prepared in the conditions applied to (a) is almost conformable with stibnite and two other modifications also are producible; and (c) One of the arsenic sulphides precipitated in the conditions similar to (a) and (b) seems not yet consistent completely with realgar but four other kinds of modifications are attainable. In the light of the whole data, it appears that, though each diffraction pattern

STUDIES ON QUICKSILVER DEPOSITS

reveals an mutually different appearance, there are none the less the transitional relations among the sulphides of quicksilver, those of antimony and those of arsenic. In the case of mercuric sulphides, for instance, the pattern of cinnabar belongs to the rhombohedral lattice, that of the higher-temperature modification to the tetragonal lattice and that of the lower-temperature one to the cubic lattice but it seems not unreasonable to consider that these differences are caused simply by extension or contraction of the similar lattices with the variation of condition, such as the elevation of temperature or the effect of hydrogen-ion and so on. On the other hand, remarkable is the fact that cinnabar believed obtainable only in alkaline medium at a higher temperature (ca. $120^{\circ}\sim 150^{\circ}$ C.) is, on the contrary, preparable similarly in acidic state at a lower temperature or even at a room temperature if the reaction-time is properly or rather considerably prolonged and, into the bargain, certain kind of blackish modification is producible at a higher temperature than for cinnabar. It, accordingly, is presumable that some of blackish varieties simply considered as metacinnabarite may belong to this higher-temperature type. Stibnite, however, can never be prepared without boiling even though the other conditions are quite similar to those necessary for the synthesis of mercuric sulphides. The conditions suitable for the precipitation of brownish orange-colored modification (identical with metastibnite) and lead-greyish one (corresponding to stibnite) are nearly similar to each other excepting that boiling is not always an indispensable requisite for preparing the former, while the latter can hardly be produced below the boiling temperature. Orange-tinged modification obtained at a room temperature yields no diffraction patterns in the course of exposing time quite same as for the other kinds of sulphides. Brownish orange-colored and orange-colored modifications may, as in the cases of two kinds of blackish mercuric sulphides, be mistaken one for the other. As to this regard, there is surely an obscurity in the table compiled by T. Kubo.⁽⁴⁰⁾ As for the arsenic sulphides, mutual variation of their diffraction patterns shows an abnormality: That is to say, there is a step indicating an amorphous phase between the yellowish modification (identical with orpiment) prepared at a room temperature or even in boiling state and three other modifications — one of which is surely realgar — produced at a higher temperature. After all, it becomes clear from the preceding data that the immersion of respective sulphides in diluted sulphuric acid including hydrogen sulphide gas at or below ca. 100° C. for a long while is most effective for their transformation to cinnabar and stibnite or probably to realgar but the last case only is yet to be ascertained.

One of the most conspicuous reality to be added may be that the transition process from the blackish mercuric sulphide prepared through ordinary manipulation to the reddish modification or, accordingly, from metacinnabarite to

cinnabar was certainly confirmed through the measurement of potential difference shown by the concentration of then-existing hydrogen-ion in the media concerned and varying with the changes of condition in the course of time and that a method to justify the presumption or expectation as to the genesis of ores in acidic media dynamically was thus given. On the other hand, it may be concluded that the transformation expected was easiest in the solution treated with 0.01 N sulphuric acid and the work done for transition in this case was appeared as the decrease of 0.0745 volts in potential difference. As to this regard, the results, deduced from x-ray diffraction patterns, that one of the blackish modifications shows the face-centered cubic lattice ($a = 5.83 \text{ \AA}$) and the brownish one the face-centered rhombohedral lattice ($a = 4.11 \text{ \AA}$, $c = 9.46 \text{ \AA}$) must be remembered. It is easily calculated from these data that the length of each edge of the rhombohedron a is 5.69 \AA and those of its face-diagonals are 8.22 \AA and 7.89 \AA , respectively. if the rhombohedron under consideration is assumed to belong to the first order. Since the distorted quantity in its diagonal plane is nearly negligible because of less than 1° of the inclination between the edge and the normal to the rhombohedral plane, the mass of the rhombohedron per unit-cell may be approximately

$$M_1 = \frac{8.22 \times 7.89}{2} \times 5.69 \times 8.1 \times 10^{-24} \text{ gr.} \\ = 1.50 \times 10^{-21} \text{ gr.}$$

where 5.69 \AA is the distance between the rhombohedral planes and 8.1 is the mean density of the brownish modification; while the mass of the blackish one prepared at a lower temperature, on the other hand, is

$$M_2 = (5.83)^3 \times 7.7 \times 10^{-24} \text{ gr.} \\ = 1.53 \times 10^{-21} \text{ gr.}$$

where 7.7 is assumed as its mean density. It, therefore, follows that

$$M_1 \approx M_2$$

If the very rhombohedron is assumed to belong to the second order, its edge is to be 6.33 \AA and face-diagonals are 9.49 \AA and 8.36 \AA in length, respectively. Nevertheless, there arise not only a considerable difference in masses but also a contradictoriness in such regard that the expansion of the unit-cell yields the increase of its density. It is also considered to be not the case with the third order on the basis of similar calculation. Comparing the rhombohedral lattice thus determined to belong to the first order with the cubic one of the blackish modification, the quantities of contraction of the latter are regarded as $(198.155 - 184.515 = 13.64) \times 10^{-24} \text{ cm}^3$ or 6.8% in volume and $(10.09 - 9.46 = 0.63) \times 10^{-8} \text{ cm}$ or 6.2% in the direction of three-folded axis of rotation or body-diagonal. It, for the present, results that the work represented by the decrease of 0.0745 volts in potential difference caused the contraction

STUDIES ON QUICKSILVER DEPOSITS

of 6.8% in volume of the blackish sulphide if rough estimation be permissible.

In consideration of the data referred to already and the potential energy of univalent face-centered cube of zincblende-type regarded roughly as $-\frac{11.12 e^2}{a}$ ⁽⁴¹⁾, it becomes possible to find the work done or to solve the question concerning the process of transition in more or less details. As pH-values increased, for example, from 2 to 3 during the reaction, about 0.007gr.—0.00069gr. = 6.04×10^{-3} gr. of hydrogen-ion are considered to have been consumed for the transformation of mercuric sulphides and the total amount of positive charges consumed, therefore, is estimated at

$$\begin{aligned} & \frac{6.04 \times 10^{-3} e}{1.67339 \times 10^{-24}} \\ = & \frac{6.04 \times 10^{-3} \times 4.8025 \times 10^{-10}}{1.67339 \times 10^{-24}} \\ = & 1.47 \times 10^{12} \text{ C. G. S. esu.} \end{aligned}$$

Since the decrease of potential difference was measured to be

$$\begin{aligned} 0.0745 \text{ volts} &= 0.0745 \times \frac{1}{300} \text{ C. G. S. esu.} \\ &= 2.483 \times 10^{-4} \text{ C. G. S. esu.,} \end{aligned}$$

the quantity of the work done may be simply electrostatically estimated at

$$2.483 \times 10^{-4} \times 1.47 \times 10^{12} \text{ ergs} = 3.65 \times 10^8 \text{ ergs.}$$

Moreover, the difference between potential energy of both modifications under consideration is assumable to be

$$\begin{aligned} & 11.12 e^2 \left(\frac{1}{a_2} - \frac{1}{a_1} \right) \\ = & \frac{11.12 \times (2 \times 4.8025 \times 10^{-10})}{10^{-8}} \left(\frac{1}{5.69} - \frac{1}{5.83} \right) \\ = & 4.30 \times 10^{-12} \text{ ergs per unit-cell} \end{aligned}$$

where two times of the value for e are here adopted because the original formula was related to univalent cube. On condition that the mass of mercuric sulphide per unit-cell is, as was already found, 1.50×10^{-21} gr. and the actually deposited amount of the very sulphide is considered to be $6.68 \text{ gr.} \times \frac{232}{270} \times \frac{15}{100}$ = 0.8684 gr., it must be that $\frac{0.8684}{1.5 \times 10^{-21}} = 5.79 \times 10^{20}$ of unit-cells are con-

tained in the precipitate and the difference of potential energy, consequently, is totalized to be $4.30 \times 10^{-12} \times 5.79 \times 10^{20} \text{ ergs} = 24.92 \times 10^8 \text{ ergs.}$

It, thus, is to be noted that considerable coincidence between the work done probably or partly, at least, by the positive charges for a slight deformation of the blackish sulphide to the reddish one in the media concerned and the difference of potential energy of both modifications were derived from these simple calculations if certain factors, for instance, the resultant values

of dielectric constant and any others were taken into consideration to some extent. It is of course that these simplifications are by no means permissible for the purpose of purely theoretical calculations because, in the essential formula concerning the potential energy of a crystal : $V = -\frac{Ac^2Z^2}{r} + \frac{Be^2}{r^12}$ (43) not only the first term derived simply from square-inverse force but also the second term connecting with the bond energy and others are of significance.

(4) Conclusion.

The undeniable fact is that both cinnabar and stibnite (presumably as well as realgar) can be prepared similarly in acidic state. It seems that sodium sulphide, when it is used, plays a role of catalyzer. But for these experimental evidences, it is difficult to interpret the results obtained from the field observations; for instance, the paragenetic relations of low temperature hydrothermal minerals or the assimilation of these minerals in pyrophyllite and other clayey minerals believed to have been derived from country rock by the action of acidic solution, especially such as sulphuric acid. Moreover, some other phenomena such as the formation of alunite or gypsum veins or pyrophyllitization and alluitization of country rock appeared in the low temperature hydrothermal deposits or in their neighborhood are at the same time deducible from these laboratory works. On the other hand, the results obtained from the experiments are not necessarily inconsistent with the example proving the deposition of cinnabar in alkaline spring because certain amount of sulphuric acid or sulphide-ion also are evidently present there.

Since cinnabar is preparable at a temperature lower than in the case of stibnite, the vertical distribution of the latter in ore deposit must be deeper than that of the former. This is agreeable with the reality in the fields and also with Emmons's zoning of ores,⁽²⁾ as to which some references were made in Part I. Even aside from the remarkable fact that the amorphous antimony sulphide and orpiment belong to the lower-temperature modifications of stibnite and realgar respectively and one of the blackish mercuric sulphides is obtainable at a temperature higher than for cinnabar, it is to be noted that all these modifications are produced simply in acidic state.

Another important factor indispensable for preparing the modifications identical with native minerals in their crystal structures is a duration of reaction-time: This may easily be deduced but has never been proved numerically by the experimental data. As a matter of fact, these circumstances are shown specifically in that cinnabar is attainable even in the state of higher acidity, for instance, in 0.1 N sulphuric acid in the course of long time at a room

STUDIES ON QUICKSILVER DEPOSITS

temperature though the elevation of temperature can of course promote the reaction.

The data of solubility purely chemically obtained for the synthesized sulphides may be almost worthless for the study of geochemical phenomena where the mutual relations among the kinds and concentration of media, the variation of temperature and the duration of reaction-time and so forth must be synthetically considered even if there arises no increase or decrease of the components in the system concerned. For instance, it is electrochemically proved that mercuric sulphides as well as other similar sulphides can be dissolved as a complex salt in considerably concentrated alkali sulphide but it seems to have been neglected that this theory is not applicable to the case of such dilution as is expected in low temperature mineralizing solution intact.

Previous concepts in connection with transition also is not thought to be essential from the geochemical or ore-depositary point of view. This is because that certain pairs or groups of modifications are mutually transformable at a temperature far lower than have ever been believed if the other conditions are properly regulated. Transition-temperature determined without consideration on the complicated variation or combination of then-existing media and on duration of time have no geochemical significance. And, since transition among various modifications can occur similarly with variation of conditions other than temperature, it may be that transition-point determined ordinarily in one-component system in a dry state is not useful for studying geological phenomena.

A subject regarding the colorization of cinnabar is remained to be clarified. Some author,⁽²⁾ ascribed the color of metallic compounds simply to the formation or structures of their complex salts from a standpoint different from Dreyer's suggestion and referred to their stability but it is evidently problematical to adhere in this opinion whereas different colored specimens such as reddish and brownish ones give quite similar configurations in their inner architectures. As to this regard, further detailed investigations must be necessary.

In concluding this argument, the writer wishes to place special emphasis on the following :

It now is generally known that there are two kinds in the methods for studying the genetic origins of ores — one is concerned directly in the mineralization process and the other in the petrogenesis. The writer, however, investigated the subjects in question mainly according to the former, believing it as better than by following the latter, because the key to the numerical — though to a slight extent — solution of the problem can thus be obtained. And, basing upon the experimental data cited in Part 2, main parts of the writer's presumption relating to the genesis of cinnabar and other paragenetic

sulphide minerals were at the same time proved to be not unreasonable.

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Hg
C Fe



(a)

Sb
C Fe



(b)

As
Fe C



(c)

Plate 52

Diffraction patterns on cylindrical films.

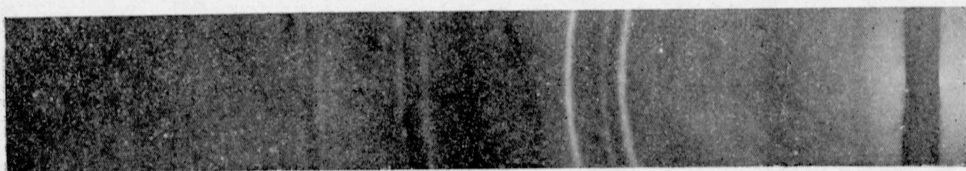


Plate 53 Cinnaber.



Plate 54 Brownish mercuric sulphide.



Plate 55 Black-colored mercuric sulphide obtained at a boiling temperature.

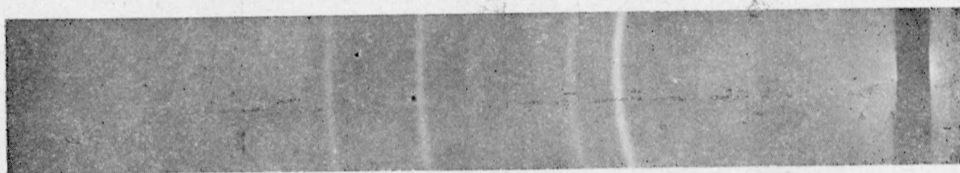


Plate 56 Black-colored mercuric sulphide obtained at a room temperature.

Diffraction patterns on flat films



Plate 57 Cinnabar. (Specimen same as Plate 53)



Plate 58 Brownish mercuric sulphide. (specimen same as Plate 54)



Plate 59 Scarlet-colored mercuric sulphide obtained by adding few drops of sodium sulphide solution and then boiling in sulphuric acid for fifty hours.

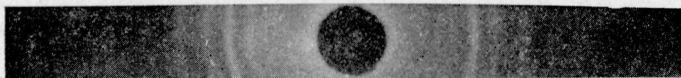


Plate 60 Black-colored mercuric sulphide prepared at a boiling temperature. (Specimen same as plate 55)



Plate 61 Black-colored mercuric sulphide obtained at a room temperature. (Specimen same as plate 56)

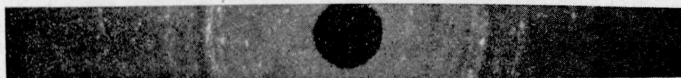


Plate 62 Stibnite



Plate 63 Lead-greyish antimonous sulphide obtained by boiling in sulphuric acid



Plate 64 Lead-greyish antimonous sulphide obtained by adding few drops of sodium sulphide solution and then roughly washed with diluted acid.

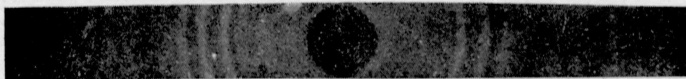


Plate 65 Brown-reddish antimonite sulphide obtained at a boiling temperature.

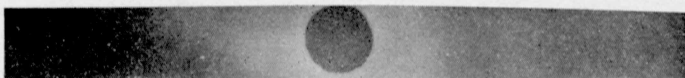


Plate 66 Orange-reddish antimonite sulphide obtained at a room temperature.

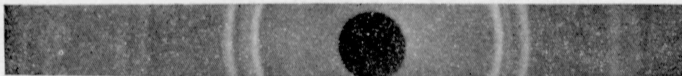


Plate 67 Realgar.

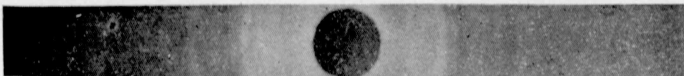


Plate 68 Cockscomb-colored arsenous sulphide obtained by adding sodium sulphide solution and warming for a week.

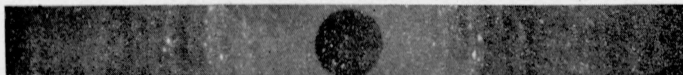


Plate 69 Vermilion-colored arsenous sulphide obtained by adding sodium sulphide solution and roughly washed with diluted acid.

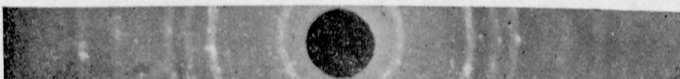


Plate 70 Yellowish arsenic sulphide prepared at a boiling temperature.



Plate 71 Yellowish arsenic sulphide prepared at a room temperature.

Fig. 17

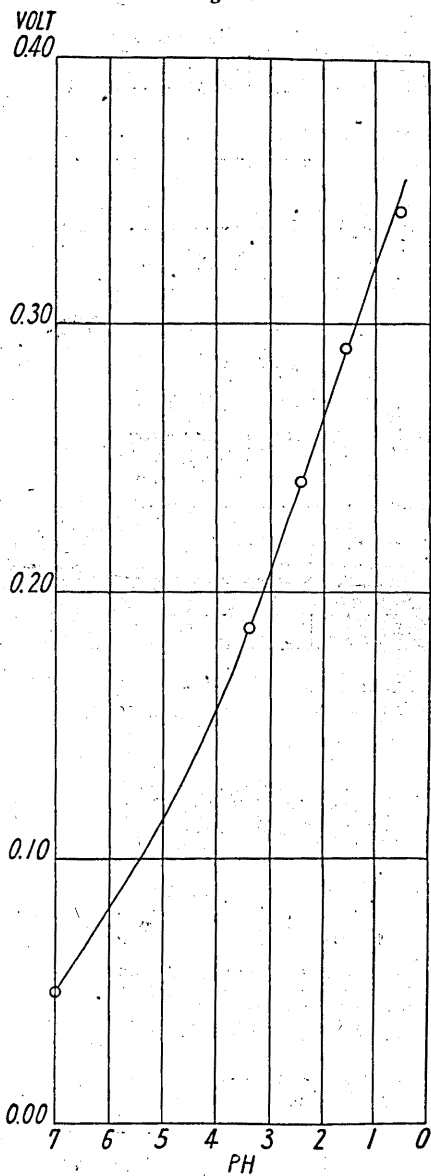


Fig. 18

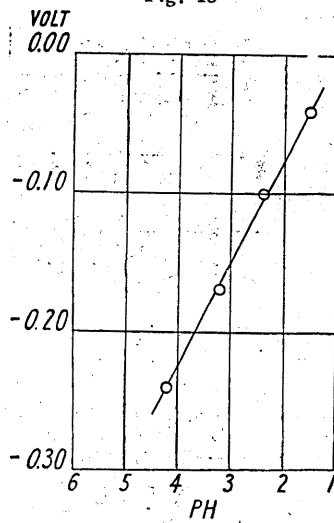


Fig. 19

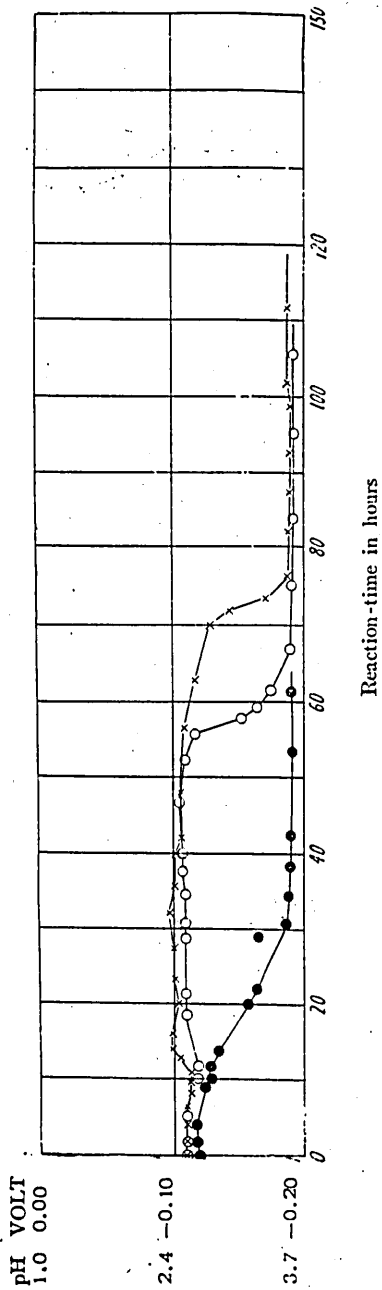


Fig. 20

