THE FORMATION OF CINNABAR-METACINNABAR AT HIDROTHERMAL CONDITIONS (BETWEEN 25° – 300°C TEMPERATURE) AND ITS GENETICAL INTERPRETATION

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Summary

Observations on natural mercury mineralizations provide controversial data about the formation $\alpha - \beta$ mercury sulfides (cinnabar-metacinnabar) as both modifications can exist in same genetical type of mineralization, which is characterised by enantiotropic temperature range. Both cubic (metacinnabar) and trigonal (cinnabar) have been recorded as first precipitations.

During the laboratory experiments sustems $HgCl_2 - H_2S - H_2O$ and $HgNO_3 - H_2S - H_2O$ have been studied in temperature range between 25° – 100 °C. Structural and morphological deformations of cubic modification formed on 25 °C have been investigated in temperatures between 50° – 300 °C.

The role of As, Sb, Tl trace elements in the formation of cinnabar-metacinnabar have also been studied.

These chemical, crystal-chemical investigations provide additional data to the genetic interprtation of mercury deposits.

Introduction

Mercury deposits have generally simple mineralogical composition, mainly consisting of $HgS - Hg - Sb_2S_3$ and few other associated elements. The deposits are characterised by the dominance od *S*, *Ca*, *Si* (*Fe*, *Mg*) and *O* elements, *As*, *Sb* and *Cu* chalcophile elements, occasional concentrations of *Au*, *Ag*, *Bi*, *Pb*, *Zn*.

The average concentration of mercury in the Earth's crust is 0, 0X ppm:

Vinogradov	(1949, 1963)	= 0,07 – 0,083 ppm
Taylor	(1964)	= 0,08 ppm

The concentration is not affected by the acidity of igneous rocks (Turekian – Wedepohl, 1961, Vinogradov, 1962 third column: Ehmann – Lovering 1967):

ultrabasites	= 0,01 – 0,0X	ppm (4 ppb)
basic	= 0,09	ppm (7 ppb)
intermediate (syenite)	= 0,0X	ppm (4 ppb)
acid (granite)	= 0,08	ppm (39 ppb)

During the late crystalization phases, the amount of Hg in pegmatites less than 0,0X ppm, increasing in kata-and mesothermalites and reaches its peak at epithermal conditions. Volcanic exhalations generally have significant mercury content.

The *Hg* concentrations is sedimentary environment:

a) shales	0,40 ppm
b) sandstones	0,03 ppm
c) carobnates	0,04 — 0,0X ppm
d) pelites	0,X ppm

Usually high *Hg* concentration is recorded in the air above mercur deposits. This fact isused as exploration tool. Organisms (algae, fishes) show few tenth of γ/kg *Hg* content.

The most important minerals of mercury are the $\alpha - \beta - \gamma - HgS$, cinnabar and metacinnabar and the native mercury. Schwazite (HgS np to 24 per cent Hg), livingstonite ($(HgSb_4S_8)$, montroydite (HgO), guadalcazzarite (HgZn) (S, Se), onophrite Hg(S, Se), coloradoite (HgTe), tiemannite (HgSe), kleinite $Hg_2N(Cl, SO_4) \cdot nH_2O$, mosesite $(Hg_2NCl \cdot H_2O$, terlinguaite $(2HgO \cdot Hg_2Cl_2)$, eglestonite (Hg_6Cl_4O) are rare accessories in mercury deposits. The oxide-chlorides are possible products of the vapor phase.

There are several opinions about the formation of cinnabar-metacinnabar:

- metacinnabar crystallises prior to cinnabar (αHgS)
- metacinnabar and cinnabar are crystallising syngenetically
- formation of metacinnabar follows that of αHgS
- metacinnabar precipitates from solutions and is not an alteration product of cinnabar
- metacinnabar has supergene origin.

In hot brines of Amadee Hot Spring, California, and Bouiking Spring, Idaho, metacinnabar (βHgS) crystallises, subsequent to cinnabar. There are examples for reversed precipitation sequences too. The formation of metacinnabar is probably affected by temperature, and probably, the pH conditions and the chemical assemblage, however the effects of there latter facter has not been experimentally proved yet. Near the month of Amadee Hot Spring precipitations, of cinnabar, metacinnabar, in onter zones drops of native mercury has been observed from the alkaline hot brines. From hot brines at Sulphur Bank California, similar phenomena have been recorded.

At Bouiling Spring (Valley County, Idaho) crystallisation of *Mn*-rich metacinnabar have been described, at 7 — 8 m distance from the mouth of the Spring. Cinnabar has formed near the mouth, associated with calomel, Hg-oxide-chloride, chalcedony, quartz, montmorillonite, alunite.

K r a u s k o p f (1951) has suggested a temperature range 80° – 250 °C at 30 at pressure for the formation of cinnabar. D i c k s o n (1964) has given 100 – 230 °C temperature at 30 at pressure. The solubility of HgS in Na_2S solution had first studied by K n o x (1906), then D i c k s o n (1964), W h i t e et al (1967) at 3·5 – 7·5 pH, 25° – 200 °C temperatures, 4 – 140 at pressures.

Based on conclusions about the $HgS - H_2O - Na_2S$ system, it seems that alkalinity has favourable effect on the formation of HgS. The $(SO_4)^{2-}$ content of alkaline hot brines (Na_2SO_4)indicates that Na_2S has an important role in solubility and transport of HgS. Based on

$$HgS + Na_2S_{(aq)} \rightleftarrows NaHgS_2 \text{ reaction,}$$

$$K \text{ is equal to } \frac{Na_2HgS_2}{(Na_2S)HgS}$$

hence Na_2S increases the solubity of HgS. Whit increasing temperature the solubity of silicates (e. g. quartz) is also increasing. This gives an explanation for the relationship of HgS mineralization and silicecus environment. The coefficients of solibility:

Cinnabar $K = 10^{-3,50}(10^{-3,51})$ (S c h w a r z e n b a c h – Widmer) Metacinnabar $K = 10^{-59}(10^{-3,60})$ (S c h w a r z e n b a c h – Widmer) The solubility of HgS in the $HgS_{(s)} - Na_2S_{(aq)}$ system is increasing from 20 °C to 100 °C, decreasing between 100° – 150 °C, then gradually increasing. At room temperature the solubility of metacinnabar is 30 per cent larger than that of cinnabar. Until the inversion teperature for metacinnabar-cinnabar (344 °C) is not reached 30 per cent of the crystalline phase is cinnabar.

The irreversibility of $HgS_{(s)} + Na_2S_{(aq)} \rightleftarrows Na_2HgS_2$ system is highly influenced by the CO_2 content and oxygene saturation of the solution. This phenomene plays inportant role in the formation of HgS and mercury deposits in carbonate environment (A l g e r i a, N e w I d r i a – USA, R ó k a h e g y – Hungary)

In the $HgS_{(s)} + 2H_2S_{(aq)} \rightleftarrows HgS(H_2S)_{2(aq)}$ system at 20 °C temperature

$K = 10^{-4,25}$ cinnabar
$K = 10^{-4,31}$ metacinnabar

In the $HgS + S^{2-} = Hg_2^{2-}$ system B a r n e s (1976) suggested

$K = 10^{+0,57}$ = metacinnabar
$K = 10^{+0,48}$ = cinnabar

These data indicate that formation of deposits composed of Hg – HgS are associated by alkaline $+ HgS_2^{2-}$ – hydrotermal solutions.

D r e y e r (1940) concluded that most HgS deposits form at near-surface conditions, on normal pressure. D i c k s o n (1964) stated that HgS mineralizations could form at low pressure (1 – 30 at) and temperature

100° — 230 °C from neutral — or slighthy alkaline solutions, because stabiliy ranges of Hg-complexes are determined by the above-mentioned physico-chemical parameters.

5 pH = $Hg(HS)_2$ less important in transport of *Hg*

6 — 8 pH = $Hg(HS)$ | most abundant *Hg*-complex

9 pH = HgS_2^{2-} |

In sulfide-complexes mercury is linked to chains with 2 or 4 coordination, these govern the development of chainstructures of cinnabar or framework structure of metacinnabar (B a r n e s et al. 1967. Fig. 1).

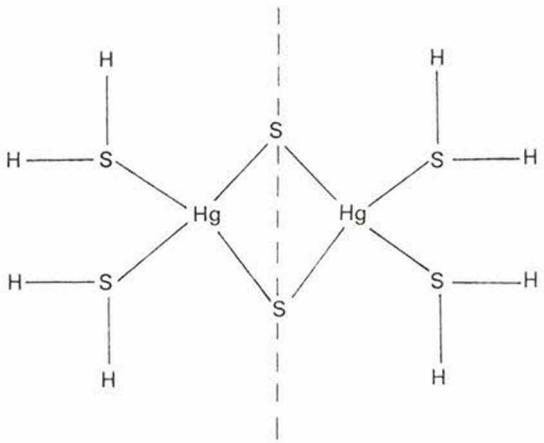


Fig. 1. Co-ordinating ligands of the HgS (B a r n e s et al.)

As indicated by several Hg-chloride minerals, transfer of mercury in chloride-complexes is also a possibility. The stability of Hg-chlorides is strongly temperature dependent, these minerals occur rarely compared to the HgS modifications, (K r a u s k o p f 1951).

The equlibrium constants of Hg-chloride complexes:

$$Hg^{2+} + Cl\ (HgCl)^{+}: K = \sim 10^{7,3}$$
$$Hg^{2+} + 4Cl (HgCl)^{2-}: K = \sim 10^{16,1}$$

Hydrothermal experiments

Laboratory experiments have been carried out in liquid-vapor and solid-liquid phase systems:

a) Synthesis of HgS monophase from solutions containing Hg^{+} and Hg^{2+} ions at 25° — 50° — 75° — 100°C temperatures

1. (0.1 mol $HgNO_{3(aq)} + H_2S_{(g)}$
2. 0.1 mol $HgCl_{2(aq)} + H_2S_{(g)}$

b) Effects of As^{3+}, Sb^{3+}, Tl^{+} on the formation of HgS (by Hg:R ratios of 100:1 and 1000:1):

1. 0,1 mol $HgCl_{2(aq)} + AsCl_3 + H_2S_{(g)}$
2. 0.1 mol $HgCl_{2(aq)} + SbCl_3 + H_2S_{(g)}$
3. 0.1 mol $HgCl_{2(aq)} + TlCl + H_2S_{(g)}$

As, Sb, Tl have been chosen as "impurities", because the stabilities of their sulfide-complexes are similar to that of HgS, atomic radii are near to that of *Hg*, and occur in epithermal ore deposit.

c) HgS ($=\beta$HgS-metacinnabar) $+ H_2O$ and $\beta HgS_{(aq)} + Na_2S_{(g)}$ systems between $25_2 - 300$ °C. HgS is synthetised from $HgCl_{2(s)} + H_2S_{(aq)}$ system at 25 °C.

d) Metacinnabar (βHgS) in solutions with composition Hg:R = 100:1 between 50° – 300 °C. (R = As^{3+}, Sb^{3+}, Tl^{+}).
Laboratory experiments are calculated with mercury ions migrating in chloride-complexes, from wich HgS phases can be formed irreversibly by the effect of $H_2S - Na_2S$ hydrotermal solutions.
Hg-ions in nitrate complexes have been investigated to study the effect of synchronous or differentiated formation of α– and βHgS.

1) 0.1 *mol* $HgNO_{3(aq)} - H_2S_{(g)}$ *system*

The experiments have been carried out from 0.1 mol mercury (I) nitrate solution with initial pH 2.3. The pH value of the solution have been modified during the reactions:

25 °C	15 min	1.00 pH metacinnabar crystallites
	60 min	0.84 pH metacinnabar crystallites
	8 hours	0,85 pH cinnabar
	20 hours	0.85 pH cinnabar
	30 hours	0.85 pH cinnabar
50 °C	60 min	0.85 pH cinnabar
	8 hours	0.85 pH cinnabar + Hg-drops
65 °C	8 hours	1,19 pH $\beta HgS > \alpha HgS$
75 °C	60 min	1.05 pH βHgS crystallites
	4 hours	1.06 pH βHgS crystallites
	8 hours	1.21 pH $\beta HgS - \alpha HgS$?
	12 hours	1.19 pH βHgS
100 °C	10 min	1.01 pH –
	60 min	1.00 pH βHgS crystallites
	8 hours	(?) 1.0 pH $\beta HgS > \alpha HgS$

* The use of mercury (I)-nitrate is supported by two factors
a) very low solubility of Hg_2Cl_2,
b) anion effects on the formation of HgS modifications.

These data indicate that acidity of solutions formed within the same time-intervals (8 hours) is larger for αHgS (pH 0.85) than for βHgS and $\beta HgS > \alpha HgS$(1.08 – 1.21 pH). Different time intervals (15 min – 30 hours) have been used for observations of transitional and accessorial phases during the experiments. It was found that formation of stabile sulphide phases is preceded by multi-phase precipitation of white or greyish-white *Hg*-compounds: ($HgNO_3 \cdot 2H_2O$; $NHg_2OH \cdot 2H_2O$ and $NHg_2(NO_3)$. The advance of the process is marked by the increasing, appearance of black and brownis-red precipitation of HgS (Table I.)

Table I.

Crystalline phases of the $HgNO_{3(aq)} - H_2S_{(g)}$-system

Temperature	Time	Colour of reaction product	Crystalline phases
25°C	15 min.	dark gray	βHgS crystallites + Hg_3, Hg_4, Hg_6, Hg_7
25°C	60 min.	black	$\beta HgS + Hg_4$
25°C	8 hours	reddish-brown	αHgS + metallic Hg drops
25°C	20 hours	brown	$\alpha HgS + Hg +$,,
25°C	30 hours	reddish-brown	$\alpha HgS +$,,
50°C	60 min.	black and gray	αHgS, Hg_4
50°C	8 hours	brown reddish brown	$\alpha HgS + (-)$
65°C	8 hours	dark-gray	$\beta HgS \gg \alpha HgS + Hg + Hg_3S_2(NO_3)$?
75°C	60 min.	black lamellae, gray	$\beta HgS + Hg_3$, Hg_4
75°C	4 hours	gray	$\beta HgS + Hg_3$, Hg_4, $Hg_3S_2(NO_3)$
75°C	8 hours	gray, grayish white	βHgS, $\alpha - HgS(?) + HgNO_3$, Hg_4
75°C	10 hours	black and gray	$\beta HgS + Hg_3$, Hg_4
75°C	12 hours	black	$\beta HgS \gg \alpha HgS + Hg_4$
100°C	60 min.	gray, black	βHgS crystallites + Hg_3, Hg_4, Hg_7
100°C	8 hours	black, pale gray	$\beta HgS \gg \alpha HgS + Hg_3 + Hg_4 + Hg_7$

$Hg_3 = HgNO_3$
$Hg_4 = Hg(NO_3)_2 \cdot 2\ H_2O$
$Hg_6 = Hg_2S_2(NO_3)$
$Hg_7 = NHg_2(OH) \cdot 2\ H_2O$

In the $Hg(NO_3)_{(aq)} - H_2S$ system the cubic βHgS had been formed first at all temperatures, along whit $HgNO_3$, $HgNO_3 \cdot 2H_2O$, $Hg(NO_3)_2 \cdot 2H_2O$ and possibly $Hg_2S_2(NO_3)$. Following the formation of $Hg_2S_2(NO_3)$ the $HgNO_3$ bonds can split, $Hg(HS)$, $Hg(HS)_2$, HgS_2^{2-} complexes and finally the poorly soluble HgS can form. No other final phases exist beside cinnabar (αHgS). The solution exhibits the greatest acidity (0.85 pH).

Pure HgS phases have been obtained at 25° – 50 °C temperature, 8 hours. At 75 °C in different time intervals (4 – 8 hours) both βHgS and αHgS + ? had been formed, herefore experiments have been repeated at 65 °C (8 hours to obtain more exact data about $\beta HgS \rightleftarrows \alpha HgS$ reaction. These experiments indicated that in the $HgNO_3 + H_2S$ system the temperature interval for contemporaneous formation of βHgS and αHgS is 50° – 65 °C:

$$\beta\ HgS \rightarrow \alpha HgS \rightarrow [\beta\ HgS + \alpha HgS] \gg \alpha\ HgS.$$

The sulphur-content of the crystalline phases in the $HgNO_3 - H_2S$ system is highly variable due to formation of mercury:

25 °C/8 hours = +0.91% Hg and
−5.65% S
25 °C/20 hours = +3,28% Hg(Hg − drops have been separated)
−20.51% S(!)
50 °/8 hours = +3.74% Hg (Hg-drops have been separated)
−30.44% S(!)

Stochiometric ratios of HgS are shown in Table VI. Stochiometric ratios (Hg:S) could not be determined precisely due to formation of metallic *Hg* and different *Hg*-nitrate complexes. (βHgS > αHgS phases formed during reactions at 65° − 75° − 100 °C/8 hours have not been analysed du to inadequate quantities of material obtained).

The c_0/a_0 cell parameters of αHgS formed at 25° − 50 °C = 2.2891 − −2.2945 Å, at 75° − 100° theses values change to 2.3015 and 2.3064 Å respectively, indicating that the cell become more elongated. The a_0 = = 5.8682 − 5.8752 Å of βHgS crystallites formed at 75 °C/60 min and 100 °C/60 min indicate less packed, while a_0 = 5.8466 − 5.8597 Å parameters obtained from ecperiments of 8 − 12 hours duration show tightly packed cells as compared indicating that the cell become more elongated. The a_0 = 5.8682 − 5.8752 Å of βHgS crystallites formed at 75 °C/60 min and 100 °C/60 min indicate (Table II and Fig. 2).

Table II

Chemical composition of the crystalline phases of the $HgNO_{3(aq)} + H_2S_{(g)}$-system

T°	Hg	S
25°C	73,63 − 79,63%	11,02 − 9,74%
50°C	81,70 − 89,43%	9,77 − 9,60%
75°C	82,80 − 88,75%	5,83 − 7,73%
100°C	71,13 − 78,89%	6,88 − 10,21%

2) $HgCl_{2(aq)} - H_2S_{(gas)}$ *system*

The initial solution was 0.1 mol Hg (II) chloride with 4.1 pH, characterised by the following thermodinamical parameters:

F° = −42.2 Kcal/mol Robert (1971)
F° = −50.53 Kcal/mol Robert (1971)

In every case 500 ml solution have been used, reactions at 25°, 50°, 75°, 100 °C with durations of 8 hours- 45 min have been studied. During the experiments acidity have significantly decreased with time and temperature (pH = 0.70 − 1.90).

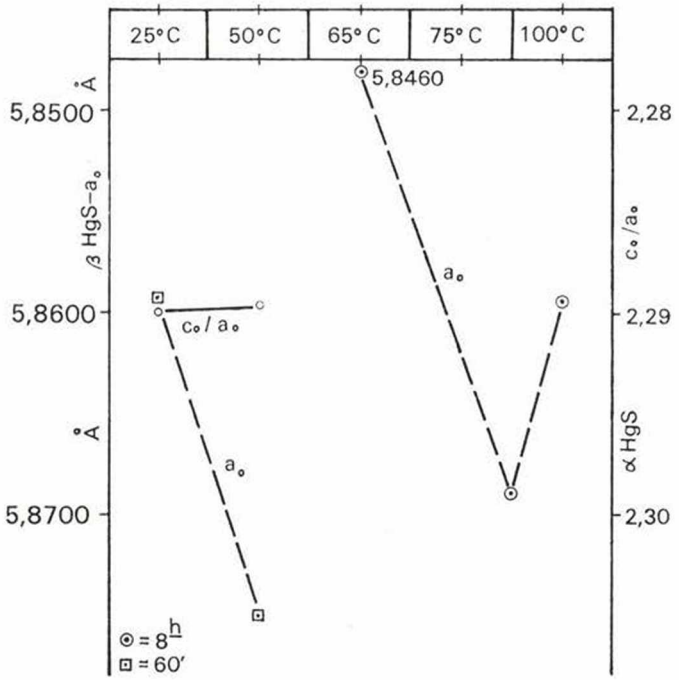


Fig. 2. $c_0/a_0 + a_0$ data of the crystalline phases of the $HgNO_{3(aq)} - H_2S$-system.

25 °C	60 min	2.35 pH	
	95 min	1.75 pH	βHgS crystallites
	8 hours	0.84 pH	βHgS
50 °C	8 hours	0.82 pH	βHgS
75 °C	8 hours	0.80 pH	βHgS$\gg\alpha$ HgS
100 °C	45 min	1.90 pH	
100 °C	8 hours	0,70 pH	βHgS$\gg\alpha$ HgS

During the reaction precipitation of white colour ($\alpha - \gamma HgS_3S_2Cl_2$) have been formed first, followed by greyish and black products. At 25° — 50 °C metacinnabar, at 75° — 100° βHgS + αHgS phases (with βHgS dominance) precipitated, associated by the following accessories:

25 °C	60 min	gray	$\alpha - \beta Hg_3S_2Cl_2$
		greyish white	
25 °C	— 95 min	*a)* greenish-grey	βHgS crystallites and
		b) pale-grey	$\alpha - \gamma Hg_3S_2Cl_2$
		c) grey	
25 °C	8 hours	black	$\beta HgS + \gamma Hg_3S_2Cl_2$
50 °C	— 8 hours	black	$\beta HgS + \gamma Hg_3S_2Cl_2$
75 °C	— 8 hours	black	$\beta HgS + \alpha HgS + \gamma HgS_3S_2Cl_2$

100 °C – 45 min	*a)* greenish grey *b)* pale-grey *c)* grey	$\alpha - \gamma\ Hg_3S_2Cl_2$
100 °C – 8 hours	black	$\beta > \alpha HgS + Hg_3S_2Cl_2$

The initial products of reactions in the $HgCl_{2(aq)} - H_2S_{(g)}$ system are the $\alpha-$ and $\gamma Hg_3S_2Cl_2$. From the two the modification has larger stability, however its presence in products of reactions at 75° – 100 °C was not observed. Unlike in the Hg(I)-nitrate – $H_2S_{(g)}$ -system, βHgS with sphalerite-type structure has been formed at 25° – 50°C temperature. At 57° – 100 °C βHgS was the dominant product, but αHgS has also ben recorded.

This indicates that in solution-vapor system the $\beta HgS \rightleftarrows \alpha HgS$ reaction takes place between 50°-and 65 °C. This has an implied explanation for controversial observations in natural systems, regarding the βHgS and αHgS precipitation sequence, (in several cases the black βHgS, in other cases the purple αHgS was recordedas first precipitation).

The formation of βHgS begin after the saturation of the solution with respect to sulphur has reached 60 per cent. Below this value of sulphur-saturation $\gamma Hg_3S_2Cl_2$ have been produced.

The chemical composition of crystalline phases of the $HgCl_{2(aq)} - HgS_{(g)}$ system (from expriments of 8 hours duration) are "richer" in Hg and S than the the products of Hg (I)-nitrate – $H_2S_{(g)}$ – system (Table III. and Fig. 3).

The data obtained from the analyses indicate that the HgS formed in the Hg(II)-chloride – H_2S system depleted in cations (Hg). but all the S-positions have been filled (?) (Table IV and VI).

Table III.

Chemical composition of the crystalline phases of the $HgCl_{2(aq)} - H_2S_{(g)}$-system

T°	Hg	S	Cl	H_2O
25°C	85,84%	13,98%	0,26%	0,00%
50°C	84,79%	14,00%	0,15%	0,03%
75°C	85,04%	13,96%	0,41%	0,07%
100°C	84,56%	13,10%	2,19%	0,04%

The a_0 structural parameter of βHgS is decreasing with the rising temperature. The c_0/a_0 parameters of the αHgS have not calculated, as only few d/Å data has been obtained.

$$25°/8h : a_0 = 5.8610\ Å$$
$$50°/8h : a_0 = 5.8408\ Å$$
$$75°/8h : a_0 = 5.8011\ Å$$
$$100°/8h : a_0 = 5.7441\ Å$$

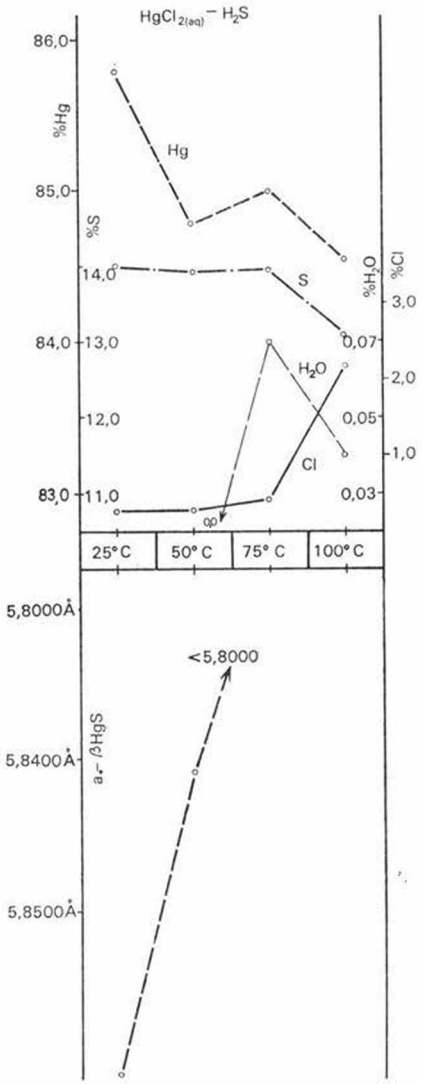


Fig. 3. Chemical composition of the crystalline phases of the $HgCl_{2(s)} - H_2S_{(g)}$ – system.

The decreasing cell-parameters of βHgS at 75° – 100 °C can be related to the initial formation of αHgS structure.

Table IV.

The non stochiometric composition of the HgS of the $HgS_{(s)} + H_2O$; Na_2S; R-chlorine systems

System	Hg				S			
	25°C	50°C	75°C	100°C	25°C	50°C	75°C	100°C
$HgNO_{3(aq)} - H_2S$	−0,91	−3,74	—	—	−5,65	−30,44	—	—
$HgCl_{2(aq)} - H_2S$	−0,42	−1,90	−1,35	−1,90	−1,30	−5,07	+1,16	−5,07
100:1								
$HgCl_{2(aq)} - AsCl_{3(aq)}\ H_2S$	−4,40	−3,27	−3,41	−1,36	+2,97	+3,55	+5,00	+5,29
$HgCl_{2(aq)} - SbCl_{3(aq)} - H_2S$	−5,22	−4,34	−3,55	−3,47	−0,07	+10,58	+5,00	+10,94
$HgCl_2 - TlCl - H_2S$	−3,93	−3,74	−2,94	−3,25	+2,25	+2,97	+4,86	+2,97
1000:1								
$HgCl_{2(aq)} - AsCl_3 - H_2S$	−0,28	−4,43	−4,47	−3,90	+1,23	+0,87	+1,74	+10,72
$HgCl_{2(aq)} - SbCl_3 - H_2S$	−0,07	−1,76	−1,04	−4,19	+2,68	+0,29	+1,09	−0,29
$HgCl_{2(aq)} - TlCl - H_2S$	−3,45	−4,44	−2,73	−4,30	+2,25	+2,39	+2,17	+3,19

3. *Experiments for recrystallization of βHgS formed at 25 °C in the temperature range between 25 – 350°C*

3.1. $HgS_{(s)} - H_2O$

The structural inversion of βHgS, which was formed in *Hg*-chloride-H_2S system has characteristic features (posthydrothermal effect structural framework diagenesis).

The crystalline product, formed at 25°C/8 hours has the following composition:

Hg	= 85.79%
S	= 14.00%
Cl	= 0.26%
H_2O	= 0,00%
	100,05%

wich is equal to

βHgS	= 97.31%
$Hg_3S_2Cl_2$	= 2.69%
	100.00%

phase-composition. The compositional changes of this product in the 25° – 300°C temperature range are shown in Fig. 4. (30 days at 25°C, 24 hours at 50° – 300°C)

The *Hg* content is decreasing with an average 1.77 per cent, while the *S* content remains practically unchanged (+0.01%). The four *Hg*-"maximum" and three *Hg*-"minimum" varies with the temperature:

Hg-"maximum" = *a)* 25°; *b)* 75°; *c)* 175° – 200°; *d)* 350°C
Hg-"minimum" = *a)* 50°; *b)* 100° – 150°; *c)* 250° – 300°C.

The *Cl* content is reducing with an average of 0,09 per cent, with the largest amount at 125° – 150°C (=0,04%, 85 per cent of *Cl* content) and at 200°C. Approximately 40 per cent of total *Cl* content can be removed without any sign of destruction. The pH factor of the solution have been stabilized at 4.82 – 3.9 between 25° – 75°C, above temperature it has become more acid at an average pH 2.24 (in the range of 2.10 – 2.37).

The inversion of βHgS to cinnabar starts at 25 °C/30 days. Between 25° – 150°C the βHgS is still the dominant phase (βHgS > αHgS), their proportion shows an opposite change between 175° – 250°C, and only mono-phase αHgS have been observed at 300° – 350° C (Fig. 5 and 6).

Using these results in the interpretation of mineral genesis it can be concluded the βHgS (metacinnabar) wich have initially crystalised from the hydrothermal solutions, can be altered to αHgS (cinnabar) at low temperatures by the effect of post-ore solutions. At higher temperatures the rate of inversion in increasing, and from 175°C the αHgS is the dominant crystal-phase. We dont have data about the rate of inversion below 175°C (It is possible that βHgS → αHgS precipitations in eocene Nummulite-limestone at Rókahegy – Budapest can be explained with this processes).

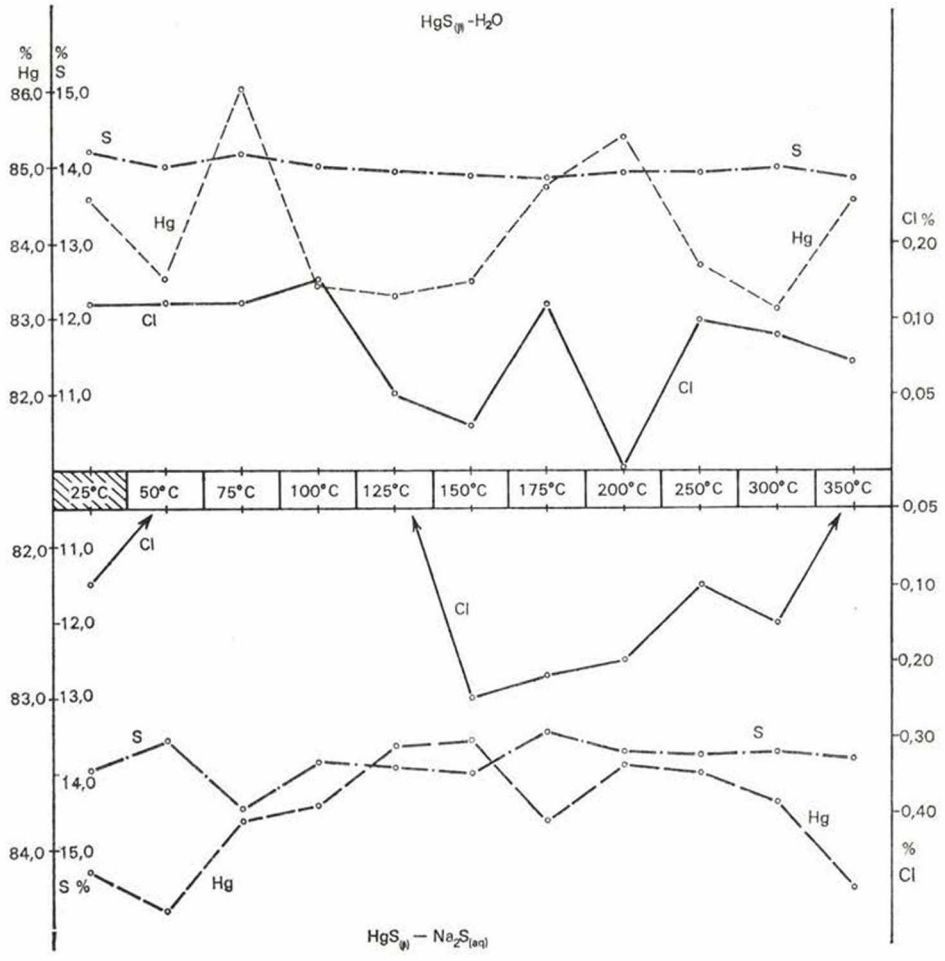


Fig. 4. The composition of $HgS_{(s)} + H_2O$ and $HgS_{(s)} + Na_2S_{(aq)}$ crystal phases as a function of T°

SYSTEM	METACINNABAR (βHgS)–CINNABAR (αHg)										
	25°C	50°C	75°C	100°C	125°C	150°C	175°C	200°C	250°C	300°C	350°C
	β > > α	β > > α	β > > α	β > > α	β > > α	β > > α	α > > β	α > > β	α > < β	α	α
HgS_{β} – $Na_2S_{(aq)}$	β > > α	β > > α	α > > β	α	α	α	α	α	α	α	α
HgS_{β} – $AsCl_3$ $_{(aq)}$	β	β	β	β	β	β	β > > α	α > > β	α > > β (?)	α	α
HgS_{β} – $SbCl_3$ $_{(aq)}$	β	β > α (?)	β > α (?)	β	β ≥ ≥ α	β ≥ ≥ α	α > > β	α > > β	α	α	α
HgS_{β} – TlCl $_{(aq)}$	β	β	β	β	β	β > > α	β > > α	β > > α	α > > β	α	α

Fig. 5. Phase relations of HgS + solution systems.
The upper line refers to the $HgS_{(\beta)} - H_2O$ system

In the non-stochiometric compositions of the $\beta HgS > \alpha HgS$ (at 25° – 150°C), the $\alpha HgS > \beta HgS$ (at 175° – 250°C) and αHgS (300° – 360°C) crystalline phases the following relationships have been observed (Table V and VI).

a) $\beta HgS > \alpha HgS$ = −0.15 − 3.33% *Hg*-deficiency and +0.94 + 4.06% *S*
b) $\alpha HgS > \beta$ HgS = −0.89 − 2.88% *Hg*-deficiency and +0.65 + 1.16% *S*
c) αHgS = −1.88 − 3.52% *Hg*-deficiency and +5.58 + 1.52% *S*

Mean values

a) $\beta HgS > \alpha HgS$ = −2.46% *Hg* + 2.02% *S*
b) $\alpha HgS > \beta HgS$ = −2.37% *Hg* + 0.84% *S*
c) αHgS = −2.70% *Hg* + 1,05% *S*

It seems that αHgS is no the average more deficient in cations than βHgS (However B a r n e s and S c o t t suggested the β HgS as *S*-deficient)

3.2. $HgS_{(s)} - Na_2S_{(aq)}$

Literature data show that the best solvent for HgS is the aqueus solution of Na_2S (D i c k s o n 1964 B a r n e s - R o m b e r g e r - S t e m p r o k − 1967). Solubility is related to the contrentration of Na_2S, at 250°C and 1800 bar has a value of 30 g/l. Phase-alterations has not been mentioned except that at temperatures below 344°C approximately 30% αHgS was formed.

The experiments in the $HgS_{(s)} - Na_2S - H_2O$ system have been initiated by the following problems:

a) the saturation of *S*-deficient position can take place diagenetically
b) if chlorine is removed the transitional reaction predict, $\gamma Hg_3S_2Cl_3$ alters to HgS,
c) what is the alteration temperature of complete inversion of βHgS to αHgS,
d) How the cell-parameters are changing during the $\beta HgS \rightarrow \alpha HgS$ alterations.

0.1 mol Na_2S solution has been used for the expreriments with the $HgS_{(s)} - Na_2S - H_2O$ system. Experiments have been carried out in Pyrex-phials, in closed system. (The duration of experiments was 30 days at 25°C, 24 hours at 50° – 350°C).

The chemical composition of the initial $\beta HgS_{(s)}$ showed the following variations during the phase alterations at 25° – 350°C (average values):

25° – 50° = −1.51% *Hg*, −0.22% *S*
75° – 300° = −2.23% *Hg*, −0.15% *S*
350° = −1.54% *Hg*, −0.21% *S*

The following Cl contents have been analysed:

150° – 200°C = 0.20 − 0.25% *Cl*
25° – 125°C = 0 − 0.10% *Cl*
250° – 350°C = 0 − 0.15% *Cl*

The pH of the solution showed slightly decreasing tendency:

$$25° - 200°C = 9.86 - 10.35$$
$$250° - 300°C = 9.58 - 8.24$$

The βHgS phase alterations in the $HgS - Na_2S - H_2O$ system indicate that $Na_2S + H_2O$ solution (post-ore hydrothermal solution) accelerates the formation of αHgS and at $100° - 350°$ exlusively mono-phase cinnabar structure is formed:

a) $25° - 50°C$ = black, $\beta HgS > \alpha HgS + \gamma Hg_3S_2Cl_2$
b) $75°C$ = brownish-red $\alpha HgS > \beta HgS + \gamma Hg_3S_2Cl_2$
c) $100° - 175°C$ = purple $\alpha HgS + NaHgCl_3 \cdot 2H_2O$
d) $200° - 350°C$ = purple $\alpha HgS + \gamma Hg_3S_2Cl_2$

(Table V., VI. and Fig 4.)
The non-stochiometric compositions of $\beta HgS > \alpha HgS$; $\alpha HgS > \beta HgS$ and αHgS:

$25° - 50°C = \beta HgS > \alpha HgS = -2.09 - 2.35\%\ Hg,\ 1.16 - 1.52\%\ S$
$75°C = \alpha HgS > \beta HgS = -1.53 - 2.23\%\ Hg,\ -0.65 + 4.9\%\ S$
$100° - 350°C = \alpha HgS = -2.26 - 3.40\%\ Hg,\ -0,07 + 1.52\%\ S$

Mean values:

$25° - 50°C = \beta HgS > \alpha HgS = -2.22\%\ Hg - 0.36\%\ S$
$- 50°C = \beta HgS > \alpha HgS = -2.22\%\ Hg - 0.36\%\ S$
$75°C = \alpha HgS > \beta HgS = -2.18\%\ Hg + 2.56\%\ S^*$
$100° - 350°C = \alpha HgS = -2.98\%\ Hg - 0.80\%\ S$

On the average αHgS shows larger *Hg* and smaller *S* deficiency than βHgS, the *Hg:S* ratio of αHgS approximates the ideal 1:1 value better than that of βHgS. The celle parameter for βHgS $a_0 = 5.8521 \pm 0.0007$ Å, is unaffected by temperature changes. The c_0/a_0 value of αHgS differs from literature data (2.30 Å) with -0.01 Å (Fig. 6).

a) The results given by the experiments in the $HgS_{(s)} - Na_2S_{(aq)}$ system indicate that effects of H_2S solutions promote splitting of $[HgS_4]$-tetrahedra of βHgS and their chain like linear rearangement (cinnabar structure). It also causes the alteration of accessorial $\gamma Hg_3S_2Cl_2$ phase to αHgS by removing *Cl*. The non-stochiometric character of αHgS becames smaller despite the number of unfilled *S*-positions being larger than of βHgS.

b) The initially formed less stabile βHgS phase alters to cinnabar quite easily, therefore αHgS is more abundant in nature. Coexisting $\alpha - \beta$ HgS indicates meta-phase transitional stage, which can explain the controversial conclusions in previous studies about the phenomene that both meta-cinnabar adn cinnabar have been observed as first precipitation.

* From data of 8 – 24 – 30 hours experiments.

Table V.

The non stochiometric composition of the HgS

System	±Hg / ±S	25°C	50°C	75°C	100°C	125°C	150°C	175°C	200°C	250°C	300°C	350°C
$HgS_{(\beta)} - H_2O$	±Hg	−1,87	−3,07	−0,15	−3,20	−3,33	−3,14	−3,36	−0,89	−2,88	−3,52	−1,88
	±S	+2,90	+2,03	+4,06	+1,52	−0,72	+0,94	+0,36	+1,16	+1,01	+1,52	+0,58
$HgS_{(\beta)} - Na_2S_{(aq)}$	±Hg	−2,35	−2,09	−2,78	−2,89	−3,32	−3,40	−2,77	−3,20	−3,14	−2,91	−2,26
	±S	+1,16	−1,52	+4,92	+0,14	+0,72	+1,52	−2,54	−0,42	−0,43	−0,97	−0,07
$HgS_{(\beta)} - AsCl_{3(aq)}$	±Hg	−3,91	−2,10	−1,73	−3,27	−1,91	−1,82	−1,47	−2,08	−2,44	−0,82	–
	±S	−3,26	+1,88	+5,00	+5,00	+5,87	+5,43	+2,46	+7,32	+7,97	+3,84	–
$HgS_{(\beta)} - SbCl_{3(aq)}$	±Hg	−0,07	−1,21	−0,38	−0,60	−2,27	−2,95	−0,53	−0,53	−1,87	−0,14	–
	±S	+0,22	+1,09	−0,22	+0,72	+1,09	+0,29	+1,38	+0,87	0,00	−0,71	–
$HgS_{(\beta)} - TlCl_{(aq)}$	±Hg	−2,77	−2,30	−2,89	−1,54	−1,35	−0,15	−1,97	−3,62	−2,97	−2,15	−2,95
	±S	−0,65	−0,22	+2,39	−1,23	−1,88	+0,29	−0,65	+0,72	+0,58	−0,94	+1,23

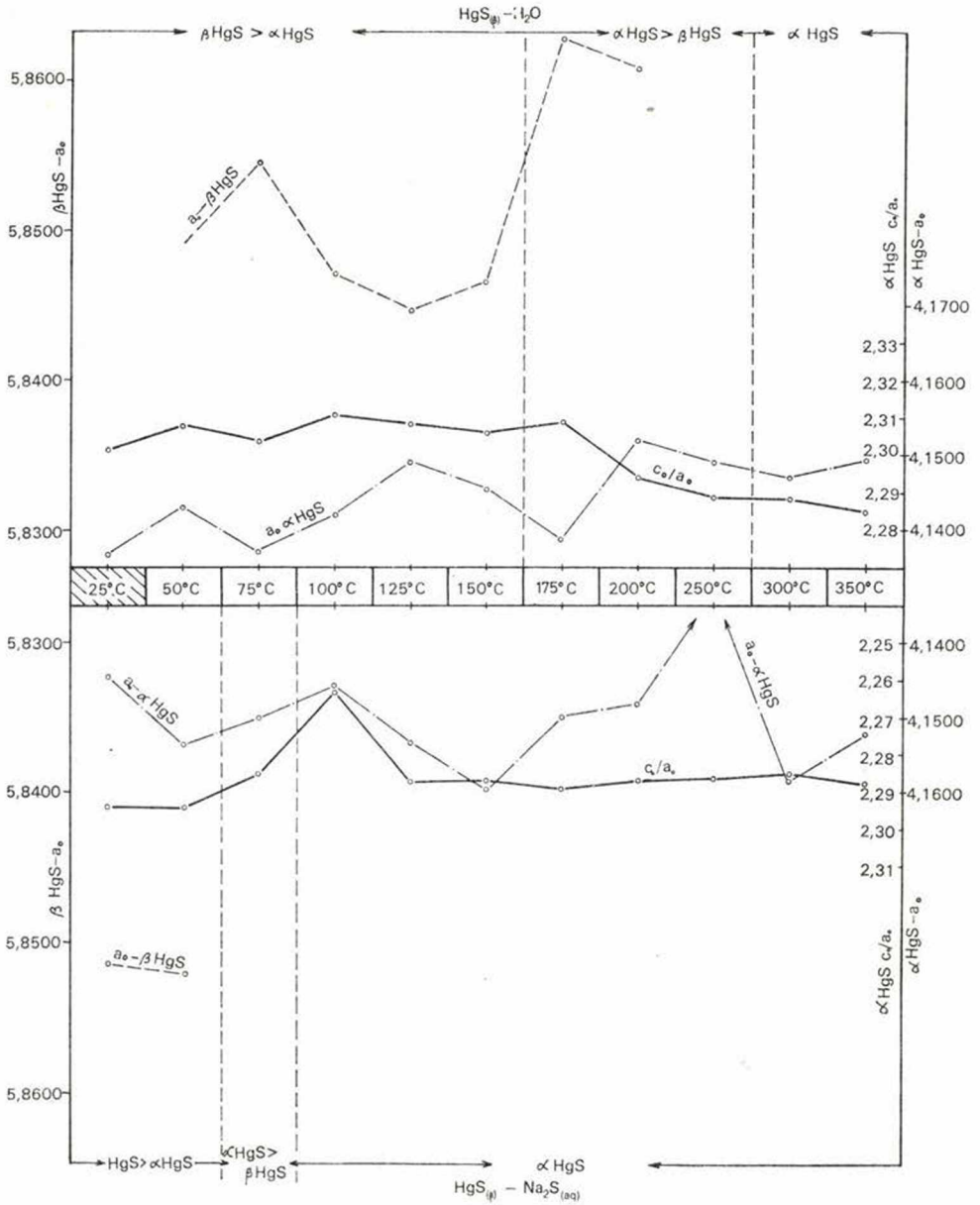


Fig. 6. Structural parameter variations of crystalphases of $HgS_{(s)} - H_2O$ and $HgS_{(s)} - Na_2S_{(aq)}$

4. *Experiments with the formation of (Hg, R) S from* $HgCl_{2(aq)}$ + *R-chloride* + H_2S *and* $HgS_{(s)}$ + *R-chloride system* (R = *As, Sb, Tl*)

4.1. $HgCl_{2(aq)} - AsCl_3 - H_2S_{(s)}$ (25°, 50°, 75°, 100°C)

a) *Hg* : *As* = 100 : 1
b) *Hg* : *As* = 1000 : 1

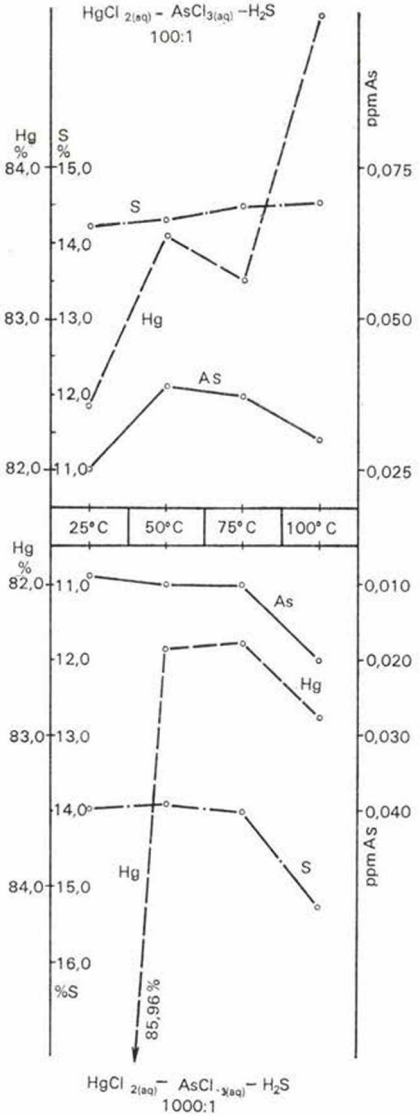


Fig. 7. Analysis data of $HgCl_{2(aq)} - AsCl_{3(aq)} - H_2S$ system

The crystalline product both systems (100:1, 1000:1) is powder-like black. The crystalline phase is βHgS, wich contained about 2 – 3 per cent $\gamma Hg_3S_2Cl_2$ impurities. It seems that with rising temperature the *Hg*, *As* and *S* exhibit little of any variation. Data of analyses are summarised in Fig. 7. The largest differences were recorded in *Hg*-content in the experiments at 25°C and 100°C. The closest correlation of *Hg-As-S* have been observed in the 1000 : 1 = Hg:As system (Fig. 7).

The average values of the analysis:

100 : 1 83.56% *Hg*; 14.38% *S*, 0.032% *As*
1000 : 1 83.38% *Hg*; 14.30% *S*; 0.012% *As*
(pH of the solution: 0.64 – 0.61)

The non-stochiometric distribution of Hg – S in crystalline phase is almost unaffected by the *As* content (Table IV., and VI).

100 : 1 *Hg* = −3.11% *S* = +4.20% *As* = 0.03%
1000 : 1 *Hg* = −3.27% *S* = +3.64% *As* = 0.01%

The largest *Hg* deficiency is in the 100:1 system at 100°C and in the 1000 : 1 system at 25°C, in βHgS phases. The βHgS cell-parameters are the smallest in this system, (average values)

100 : 1 = 327,5 ppm *As*, a_0 = 5.8396 Å
1000 : 1 = 122,5 ppm *As*, a_0 = 5.8415 Å

The difference between Hg° = 1.51 Å and As° = 1.48 Å is small, hence substition does not necessarily cause change in the cell parameters. However, the larger difference between Hg^{+} = 1.10 Å and As^{3+} = 0.58 Å caused cell contraction at 100 – 300 ppm *As* content.

The 100 : 1 system contains 327.5 ppm *As*, this explains the small average a_0 values in βHgS. Fig 8. shows that a_0 values are smaller than literature data and among the experimental data the smallest values have been obtained by no means in this system.

4.2 $HgS_{(s)} + AsCl_{3(aq)}$ – *100 : 1*

The crystalised products of the $HgS_{(s)} - AsCl_{3(aq)}$ system can be grouped in distinct temperature intervals. The mean values of analysis are arranged according the increasing temperature (Fig. 9).

a) 25 – 150°C = βHgS
b) 175°C = βHgS > αHgS
c) 200 – 250°C = αHgS > βHgS
d) 300°C = αHgS

a) 25° – 150°C = 84.08% *Hg*, 14.08% *S*, 20 ppm *As*
(pH = 1.56 – 1.67)
b) 175°C = 84.93% *Hg*, 14.14% *S*, 15 ppm *As*
(pH = 1.36)

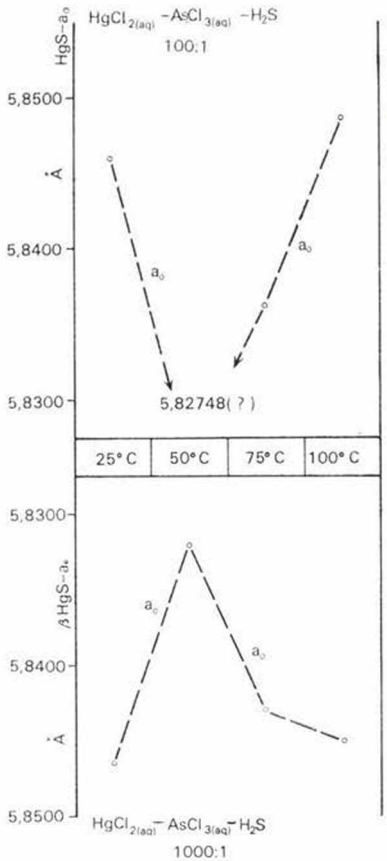


Fig. 8. Cell-parameters in $HgCl_{2(aq)} - AsCl_{3(aq)}$ – system

c) 200 – 250°C = 84.26% *Hg*, 14.86% *S*, 12,5 ppm *As* (pH = 1.36)
d) 300°C = 85.49% *Hg*, 14.33% *S*, 10.0 ppm *As* (pH = 1.45)

With increasing temperature the crystalline phases which contain 97 – 98% HgS show relative increase of HgS content and decreasing of *As*. The *Hg*-deficiency is decreasing the *S*-surplus is increasing contemporaneously, with the following average values in $\alpha HgS - \beta HgS$ phases:

a) 25° – 150°C = −2.46% *Hg*, +4.61% *S* 20 ppm *As*,
b) 175°C = −1.47% *Hg*, +2.96% *S* 15 ppm *As*,
c) 200° – 250°C = −2.26% *Hg*, +7.64% *S* 12.5 ppm *As*,
d) 300°C = −0.82% *Hg*, +3.84% *S* 10.0 ppm *As*,
(from Table V).

Table VI.

The non-stochiometric composition of the HgS

System	βHgS		αHgS		βHgS> αHgS		αHgS> βHgS	
	±Hg	±S	±Hg	±S	±Hg	±S	±Hg	±S
$Hg(NO_3)_{(aq)} - H_2S$	–	–	+3,97	−23,05(!)	–	–	–	–
$HgCl_{2(aq)} - H_2S$	−1,33	+1,38	–	–	−1,65	−3,91	–	–
$HgCl_{2(aq)} - AsCl_{3(aq)} - H_2S$	−3,19	+3,80	–	–	–	–	–	–
$HgCl_{2(aq)} - SbCl_{3(aq)} - H_2S$	−5,22	−4,34	–	–	–	+8,50	–	–
$HgCl_{2(aq)}TlCl_{(aq)} - H_2S$	−3,71	+2,79	–	–	−3,51	+2,68	–	–
$HgS_{(\beta)} - H_2O$	–	–	−2,70	+1,05	−2,46	+2,03	−2,38	+0,84
$HgS_{(\beta)} - Na_2S$	–	–	−2,98	+1,09	−2,22	+0,18	−2,51	+2,14
$HgS_{(\beta)} - AsCl_3 - H_2O$	−2,29	+4,24	−1,63	+5,91	−1,47	+2,46	−2,08	+7,32
$HgS_{(\beta)} - SbCl_3 - H_2O$	−0,68	+0,60	−1,01	−0,71	−2,61	+0,69	−0,53	+1,13
$HgS_{(\beta)} - TlCl - H_2O$	−2,17	+0,40	−2,54	+1,09	−1,91	+0,36	−2,97	+0,58

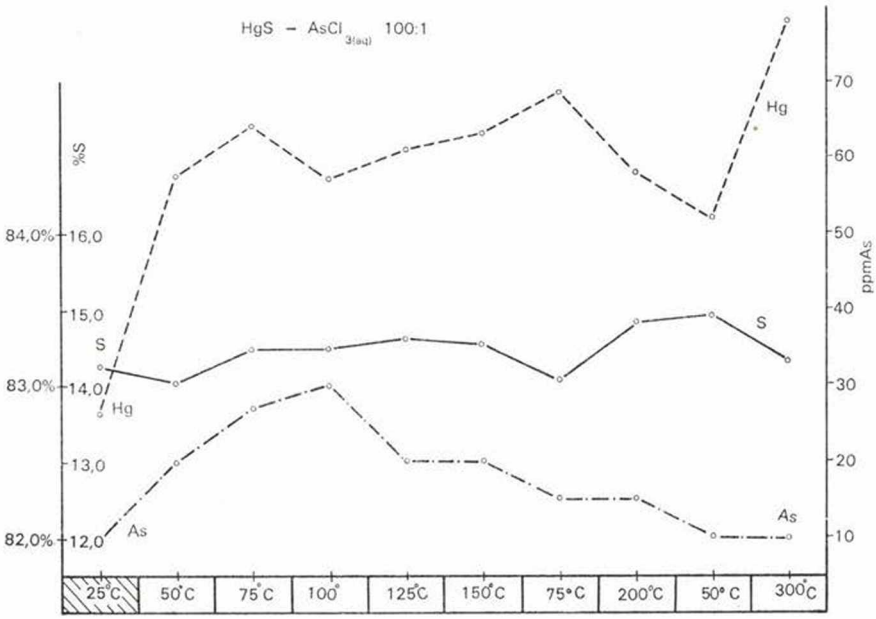


Fig. 9. Analysis of $HgS_{(s)} - AsCl_{3(aq)}$ as a function of T°

The crystalline product of reactions at 25° – 150°C is dominantly βHgS, with 1 – 2 per cent of $\gamma Hg_3S_2Cl_2$ impurities. βHgS > αHgS has been formed at 175°C, αHgS > βHgS between 200°C and 250°C, pure αHgS at 300°C. From the pure phases, βHgS is an average more deficient in *Hg – S* than αHgS (Table VI).

The cell-dimensions of βHgS are probably effected by the *As* content. The a_0 value of βHgS formed from solutions is smaller than those published in literature. After recrystalisation of the $HgS_{(s)} - AsCl_{3(aq)}$ system fall closer to these data. The values are increasing on higher temperatures:

$$\begin{aligned} 100:1\ (25° - 100°C) &= a_0 = 5.8396\ \text{Å} \\ 1000:1\ (25° - 100°C) &= a_0 = 5.8415\ \text{Å} \\ (175°C) &= a_0 = 5.8545\ \text{Å} \end{aligned}$$

The cell of αHgS formed along with βHgS is more elongated than the c_0/a_0 of that one formed as mono-phase.

$$\begin{aligned} \beta HgS > \alpha HgS &= c_0/a_0 = 2.2918\ \text{Å} \\ \alpha HgS > \beta HgS &= c_0/a_0 = 2.2909\ \text{Å} \\ \alpha HgS &= 2.2885\ \text{Å} \end{aligned}$$

Results are summarized in Fig. 10.

4.3. *$HgCl_{2(aq)} - SbCl_{3(aq)} - H_2S$ (25° – 50° – 75° – 100°C)*

a) Hg : Sb = 100 : 1
b) Hg : Sb = 1000 : 1

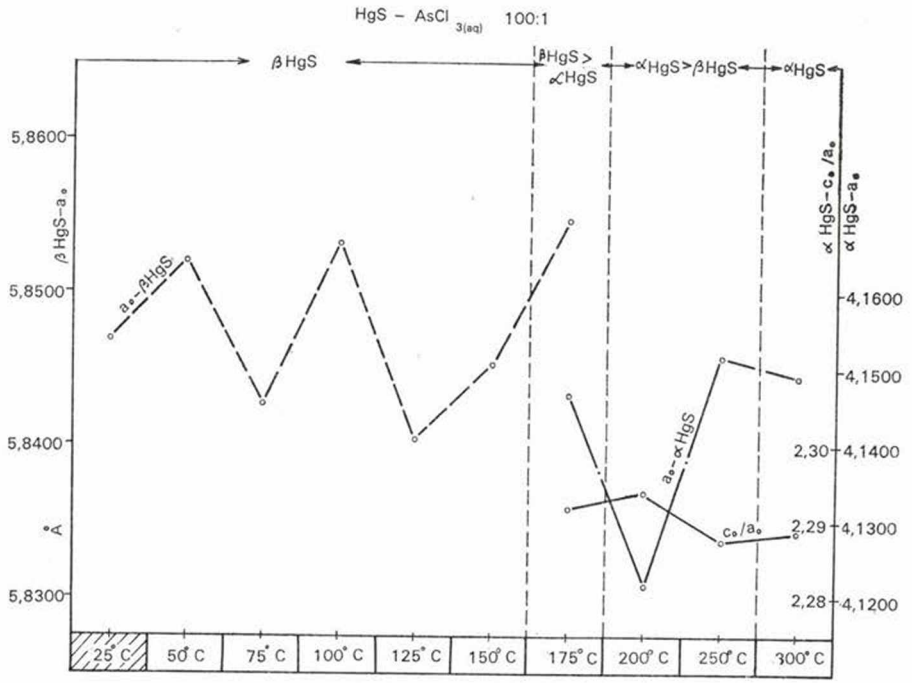


Fig. 10. Cell-parameters of crystalline-phases of $HgS_{(s)} - AsCl_{3(aq)}$ system

The antimony is the most abundant element associated with mercury mineralizations. Thus it seems reasonable to study the relationships of *Hg*-sulphides and antimony. The differences of atomic and ionic radii of the two elements:

$$\Delta = 0.15 \text{ Å (atomic radii)}$$
$$\Delta = 0.34 \text{ Å (ionic radii)}^*$$

The metallic bonds of the two element might not cause considerable change in the structural framework while with ionic linkage structural distortions possibly arise.

Black, isometric, nearly square- or diamond shaped crystallites have been formed in the systems 100 : 1 and 1000 : 1 = Hg : Sb

100 : 1

25°C	black	βHgS	pH = 0.2
50°C	black	βHgS	pH = 0.2
75°C	black	βHgS	pH = 0.2
100°C	black	β>αHgS	pH = 0.2

* = 0,22 Å at Whittaker – Muntus (1970)

1000 : 1

25°C	black	βHgS	pH = 0.2
50'C	black	βHgS	pH = 0.2
75°C	black	$\beta > \alpha$HgS	pH = 0.2
100°C	black	$\beta > \alpha$HgS	pH = 0.2

The monophase character of βHgS formed at 25° – 50°C is typical to the $HgCl_{2(aq)} - SbCl_{3(aq)} - H_2S$ system (Similar to the $HgCl_2 - H_2S$ system). From 75°C αHgS has also appeared, unlike with *As*. The amount of $\gamma Hg_3S_2Cl_2$ phase was ordes smaller than in the $HgCl_{2(aq)} - AsCl_{3(aq)} - H_2S$ system. The analysis of crystalline phases are shown in Fig. 11. This indicates that there is close relationship between *Sb – S* in both system and among *Hg – Sb – S* in the 1000 : 1 = Hg : Sb system.

The *Hg*-deficiency of the crystalline phase is larger in the 100 : 1 system than in the 1000 : 1 system. Significant variation in *S* content has been observed (Fig. 11., Table IV). The average non-stochiometric compositions.

100 : 1	= 82.62% *Hg*;	14.71% *S*;	0,77% *Sb*
1000 : 1	= 84.67% *Hg*;	13.93% *S*;	0.05% *Sb*

with differences of

100 : 1	= −4.15% *Hg*;	+6.66% *S*
1000 : 1	= −1.47% *Hg*;	+1.06% *S*

The greatest *Hg*-deficiency has been resulted in 100 : 1 system at 25°C and in 1000 : 1 system at 100°C. The *S* content in the 100 : 1 system has varied lin the range of −0.07, +10,94 (Table IV., and VI).

The βHgS formed at 25° – 100°C show cell dimensions nearly similar to literature data (being smaller, differs only in the third decimal):

100 : 1	= βHgS	= a_0 = 5.8472 Å	= 7700 ppm *Sb*
1000 : 1	= βHgS	= a_0 = 5.8483 Å	= 500 ppm *Sb*

The deformational effect of antimony can not be proved here. The distributions of cell parameters of βHgS follow similar trends both in system (100 : 1 and 1000 : 1), and show minimum at 100°C. (Fig. 12.)

4.4 $HgS_{(s)} - SbCl_{3(aq)} - 100 : 1$

Mono-phase βHgS has formed at 25° – 100°C, αHgS between 250° – 300°C, and mixed phases in 100°C – 250°C temperature range.

a) 25 – 100°C = βHgS*
b) 125 – 150°C = βHgS > αHgS
c) 175 – 200°C = αHgS > βHgS
d) 250 – 300°C = αHgS

* Formation of αHgS in form of crystal nuclei has probably started at 50 °C, but its presence is still uncertain at 75 °C.

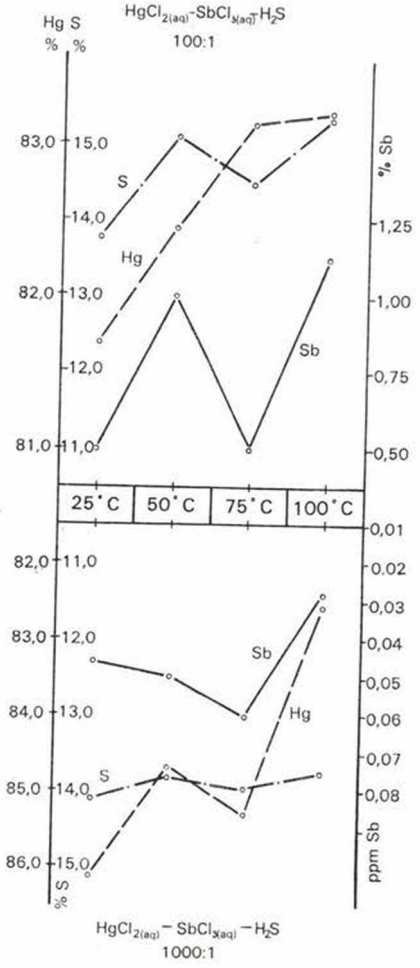


Fig. 11. Analysis data of $HgCl_{2(aq)} - SbCl_{3(aq)} - H_2S$ systems

1 – 2% $Hg_3S_2Cl_2$ is permanently present. From 75°C Sb_2S_3 was observed.

The *Hg* : *Sb* ratio in the composition of crystallized material showed inverse relationships, antimony crystallises dominantly as separate phase (Sb_2S_3), and its incorporation to the HgS structure is restricted.

The average of analysis results based in the distubution of β- and αHgS phases:

a) 25° – 100°C = 85.74% *Hg*, 13.86% *S*, 2800 ppm *Sb*
b) 125° – 150°C = 83.95% *Hg*, 13.89% *S*, 300 ppm *Sb*
c) 175° – 200°C = 85.74% *Hg*, 13.83% *S*, 30 ppm *Sb*
d) 250° – 300°C = 85.28% *Hg*, 13.85% *S*, 10 ppm *Sb* (Fig. 13.)

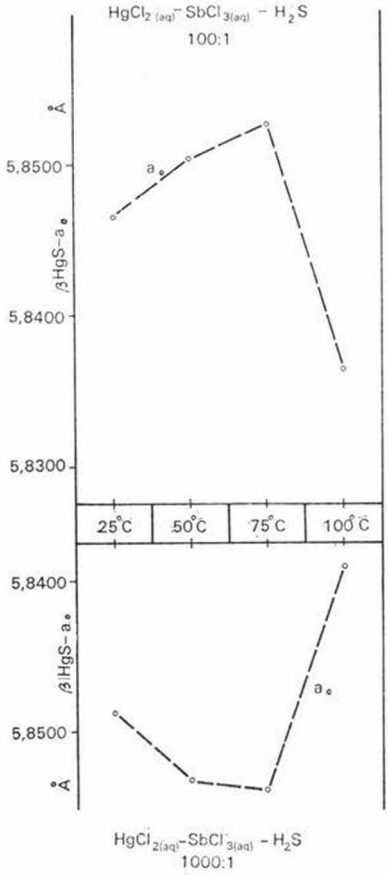


Fig. 12. HgS cell-parameters
in the $HgCl_{2(aq)} - SbCl_{3(aq)} - H_2S$ systems

The $HgS_{(s)} - SbCl_3$ system shows the smallest *Hg*- and *S* deficiency. The Hg : S ratio exhibits close relationship with stochiometric values (based on data from Table V and VII).

$$
\begin{aligned}
&a)\ \ 25° - 100° = 0{,}76\ Hg, \quad +0.60\ S\\
&b)\ 125° - 150° = -2.61\ Hg, +0{,}64\ S\\
&c)\ 175° - 200° = -0.53\ Hg, +1.13\ S\\
&d)\ 200° - 300° = -1.00\ Hg, -0.35\ S
\end{aligned}
$$

Above 200°C the $HgS_{(s)} + SbCl_{3(aq)}$ system is characterised by α HgS phases having a special crystal-morphology. The average size of crystal grains is 0.2 — 0.5 mm with maximum of 1.0 mm. The antimony catalyses the inversion of βHgS to cinnabar signyficantly. At 300°C the rate of *Sb* impurity is only 10 ppm.

The a_0 parameter: of the metacinnabar (βHgS) phases form $HgS_{(s)}-SbCl_{3(aq)}$ system averaging the following values:

a) 25°C–100°C $= a_0 = 5.8457$ Å, 2800 ppm *Sb*
b) 125°C–150°C $= a_0 = 5.8542$ Å, 200 ppm *Sb*
c) 175°C–200°C $= a_0 = 5.8563$ Å, 30 ppm *Sb*

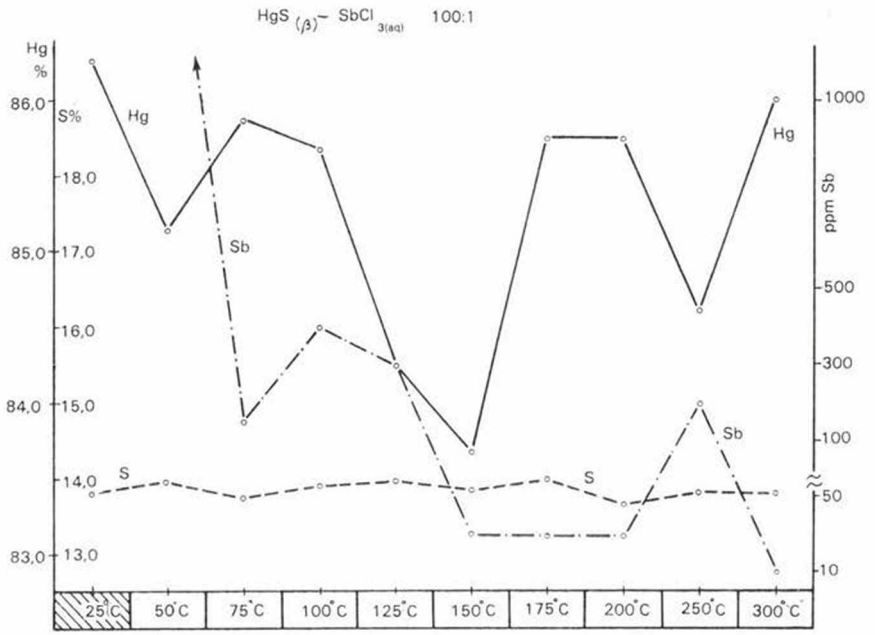


Fig. 13. Analysis data of crystalline phases of $HgS-SbCl_{3(aq)}$ as a function of T°

It seems that αHgS contains less *As* and *Sb* than βHgS with sphalerite-structure. The distributions of structural parameters of βHgS and αHgS are summarized in Fig. 14.

4.5. $HgCl_{2(aq)}-TlCl_{(aq)}-H_2S(25°-50°-75°-100°C)$

a) $Hg : Tl = 100 : 1$
b) $Hg : Tl = 1000 : 1$

Both mercury and thallium tends to cancentrate in epithermal deposits but only few data had been published about their genetical, geo-chemical relationship. For crystal-chemical reasons thallium has favourable characteristics to be in close assotiation with mercury. There is only minute difference between the atomic radii:

$$Hg^{\circ} = 1.51 \text{ Å}, \quad Tl^{\circ} = 1.60 \text{ Å} \quad \Delta = 0.09$$

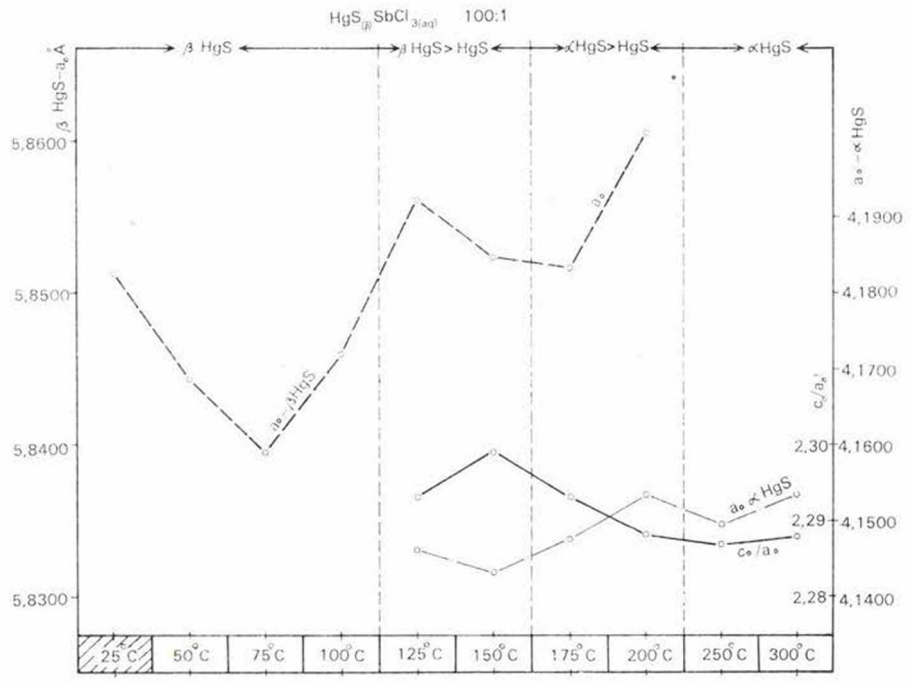


Fig. 14. Structural parameters of phases in $HgS_{(s)} - SbCl_{3(aq)}$ systems

The differences of ionic radii still permit isomorphous substitution:

$$Hg^{2+} = 1.10 \text{ Å}, \quad Tl^{+} = 1.47 \text{ Å} \quad \Delta = 0.37 \text{ Å}^*$$

The products of 100 : 1 and 1000 : 1 systems are black isometric, nearly square-sphaped grains and lamellae. At larger *Tl*-content (100:1) only βHgS has been formed. In 1000 : 1 = Hg : Tl system at 75° – 100°C αHgS has also appeared, similarly to the $HgCl_2 - H_2S$ system:

100 : 1

25°C =	black	βHgS	pH = 1.30
50°C =	black	βHgS	pH = 1.31
75°C =	black	βHgS	pH = 1.35
100°C =	black	βHgS	pH = 1.25

1000 : 1

25°C =	black	βHgS	pH = 1.30
50°C =	black	βHgS	pH = 1.30
75°C =	black	$\beta > \alpha$HgS	pH = 1.29
100°C =	black	$\beta > \alpha$HgS	pH = 1.20

$\gamma Hg_3S_2Cl_2$ as associated phase has appeared only at 100°C in the 1000 : 1 system. In other cases only HgS has been crystallised. The chlorine content

* Δ = 0.48 Å at Whittaker – Muntus (1970)

of the crystalline phases is averaging at 0.11%, in few cases 0.05% or less has been analysed. From all Hg-solution-vapor systems studied the HgS phases of the $HgCl_{2(aq)} - TlCl_{(aq)}$ system showed the highest deficiency in *Hg* and *S*, though Hg : S ratio is more permanent in this system than in ohters.

Maximum *Hg*-content has been recorded in sulphide phases at 75°C. in both systems (100 : 1 and 1000 : 1).
The Hg : S ratio is the closest to stochiometric ratios in this case. Analyses are summerised in Fig. 15.

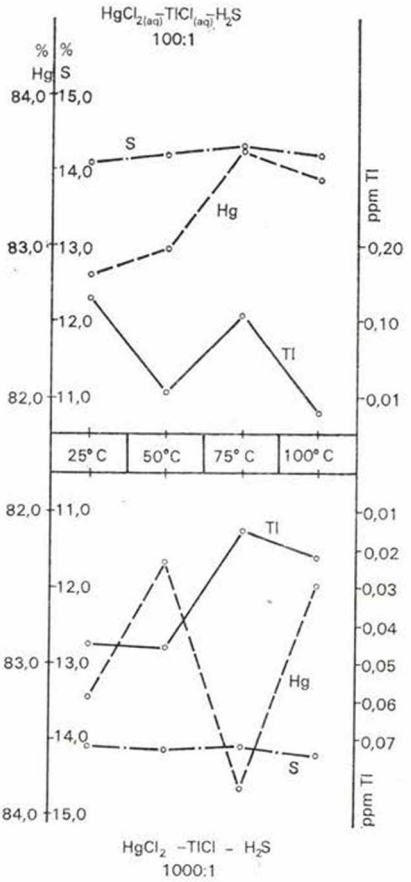


Fig. 15. Analysis data of the phases from $HgCl_{2(aq)} - TlCl_{(aq)} - H_2S$ systems

The crystalline phases show *Hg* deficiency and *S* surplus with permanent difference. (Table IV).

The average of analysis data:

100 : 1 = 83.24% *Hg*, 14.25% *S* 800 ppm *Tl*
1000 : 1 = 25° — 50° = 82.80% *Hg*, 14.12% *S*, 460 ppm *Tl*
= 75° — 1000° = 83.17% *Hg*, 14.51% *S*, 180 ppm *Tl*

wich is equal to:

100 : 1 = — 3.47% *Hg*, +3.34% *S*
1000 : 1 = 25° — 50°C = —3.99% *Hg* + 2.32% *S*
75 — 1000°C = —3.02% *Hg* + 2.68% *S*

deficiency and surplus.

The cell-parameter of βHgS phase is averagely larger than the literature data in the second decimal. As smallest a_0 values have been obtained with *As*, the largest ones with *Tl*, it is suggested that cell-deformation effect of ionic radii *Tl* > *Sb* > *As*, have been responsible for theses differences in case of ionic bonds:

100 : 1 = βHgS = a_0 = 5.8627 Å — 800 ppm *Tl*
1000 : 1 = βHgS = a_0 = 5.8506 Å — 460 ppm *Tl*

The variation of a_0 values is shown in Fig. 16.

4.6 $HgS_{(aq)} - TlCl_{(aq)} - 100 : 1$

During the experiments mixed $\beta > \alpha$ and $\alpha > \beta$ HgS phases have been formed in wide temperature interval (150° — 250°C):

a) 25° — 125°C = βHgS pH = 4.56 — 2.56 (black)
b) 150° — 200°C = βHgS > α HgS pH = 2.65 — 2.52 (black)
c) 250°C = αHgS > β HgS pH = 2.50 (brownish-red)
d) 300° — 350°C = βHgS pH = 2.57 — 2.60 (purple).

With rising temperature the acidity of the solution is increasing, βHgS is converting to αHgS. The *Hg*-content of sulfide phases shows maximum 100° — 150°C and minimum at 200°C. (Fig. 17).

The *Tl* content is gradually decreasing with temperature, while the amount of *S* remains practically unchanged. (Table V and VI).
The average values of analysis data shown in Fig. 17.

a) 25° — 125°C = 84.33% *Hg*, 13.76% *S* 400 ppm *Tl*
b) 150° — 200°C = 84.55% *Hg*, 13.81% *S* 200 ppm *Tl*
c) 250°C = 83.64% *Hg*, 13.88% *S* 70 ppm *Tl*
d) 300° — 350°C = 84.01% *Hg*, 13.95% *S* 100 ppm *Tl*

wich are equal to:

a) 25° — 125°C = —2.16% *Hg* —0.53% *S*
b) 150° — 200°C = —1.91% *Hg* +0.04% *S* (*)
c) 200°C = —1.91% *Hg* +0,04% *S* (*)
d) 300° — 350°C = —2.55% *Hg* +1.08% *S*

* based on one analysis only

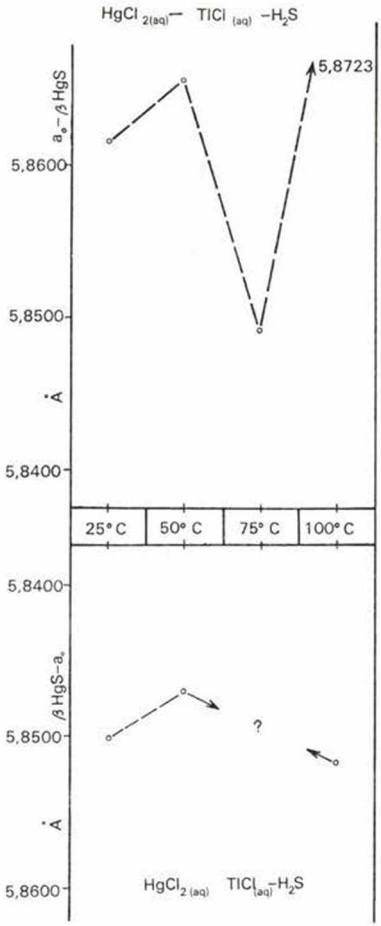


Fig. 16. Variation of cell-parameters in $HgCl_{2(aq)} - TlCl_{(aq)} - H_2S$

These data indicated as temperature was increasing (150° – 200°), the difference in *Hg* : *S* becoming smaller, then after αHgS became dominant, the difference was again larger (Table V.).

The cell-parameters of βHgS has been the largest among the systems studied:

a) 25° – 125°C = a_0 = 5.8646 Å – 400 ppm *Tl*
b) 150° – 200°C = a_0 = 5.8614 Å – 200 ppm *Tl*
c) 250°C = a_0 = 5.8613 Å – 70 ppm *Tl*

With rising temperature the a_0 values are decreasing along with the *Tl* content.

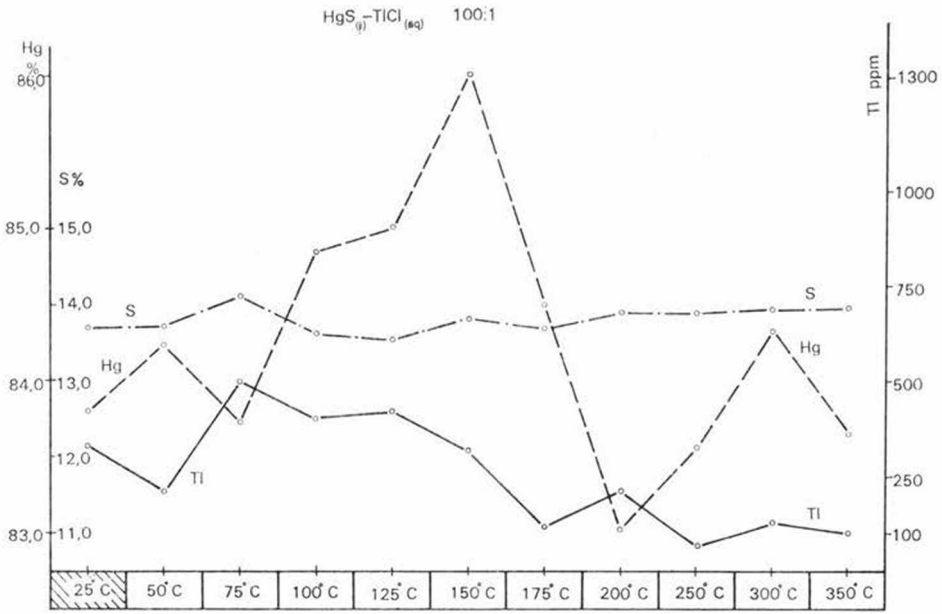


Fig. 17. Analysis data of crystalline phases of the $HgS_{(s)} - TlCl_{(aq)}$ system as a function of T°

The a_0 and c_0 parameters of αHgS are larger then literature data (= 2.91 Å), and indicate sligt elongation in c_0 direction:

150°C – HgS, c_0/a_0 = *2.305*; 175°C = *2.298*; 200°C = *2.295* Å
250°C – HgS, c_0/a_0 = *2.292*; 300°C = *2.287*; *350*°C = *2.286* Å

The variations of βHgS and αHgS cell parameters are shown in Fig. 18.

5. Conclusions

The experiments have provided new explanations for the conditions of formation of βHgS and αHgS and the crystal-chemical mechanism of their conversion. The following problems had to be answered.

1. Why both modifications were usually formed in one paragenetical sequence, and which is the primarily precipitated mercury-sulfide, βHgS or αHgS.

2. Is the βHgS of shalerite-type structure the more metastabile variety ?

3. Is there any possibility for conversion of cinnabar to metacinnabar below the temperature of the inversion point (344°C).

4. Which of the crystal-chemical data are caracteristic for βHgS and αHgS phases.

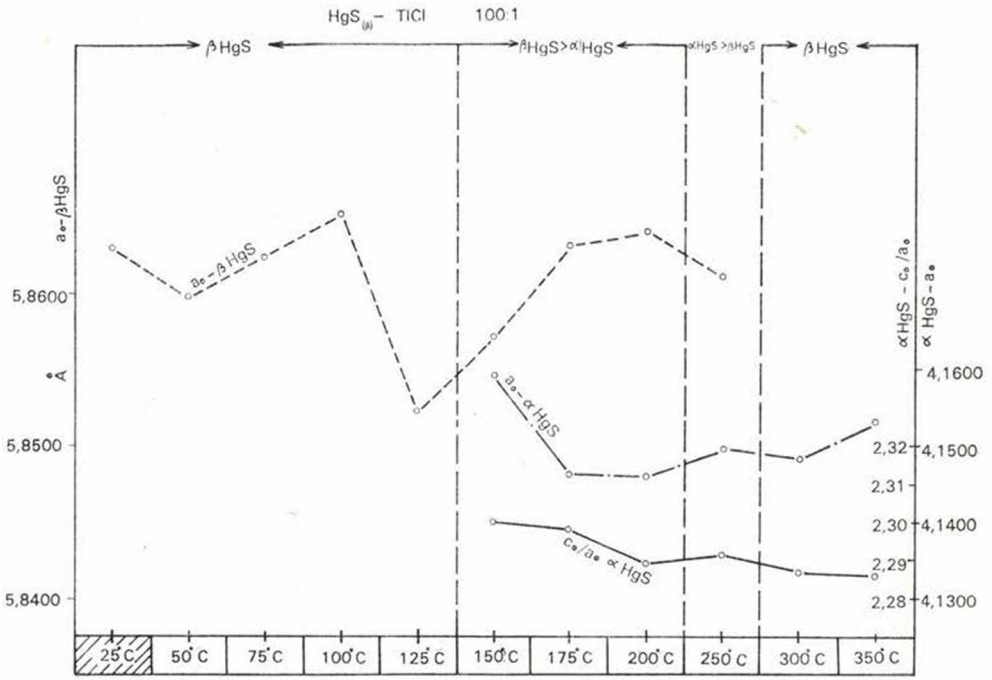


Fig. 18. Metacinnabar and cinnabar cell-parameters in the $HgS_{(s)} - TlCl_{(aq)}$-system as a function of T°

5. Is there any role of the *As*, *Sb*, *Tl* impurities applied in the experiments on the formation of βHgS and αHgS. Do they have any effect on the cell-parameters?

6. What are the preconditions of alteration of βHgS to αHgS at room temperature. The aqueons media or the Na_2S solution in wich βHgS has higher solubility is the more favourable solvent for this alteration?

This questions have been remained in most part unanswered in the previons literature of Hg-sulphide mineralization.

a) Between 25° – 75°C. The mercury, mobilized in form of complexes by chloride the most abundant anion of hydrothermal solutions crystallises as βHgS of sphalerite-type structure. The coexistent crystallistion of βHgS and αHgS in the temperature range of 75° – 100°C indicates that the formation of the more stable cinnabar-structure dies not begin at room temperatures. In the 75° – 100°C experiments only βHgS had been produced in the first short intervals, i.e. 15 – 60 min. Only initial crystallites of αHgS has developed in the 8-hours experiments, as evidencenced by the presence of the most intense 3.59 d/Å line and 1.735 d/Å doublet close to the 1.764 d/Å line of metacinnabar on the X-ray diffractograms.

From mercury (I)-nitrate solutions however αHgS, cinnabar has been formed at 25° – 50°C, suggesting that the orbital character of the Hg/I/-nitrate complex has governing effect on the development of structural type of mercury-sulfide.

In the experiments with $HgNO_{3(aq)} - H_2S$ at 75° – 100°C abrupt changes have been recorded in the propertion of mercury-sulfide polymorphs (= βHgS > αHgS). The test had been repeated at 65°C and similar, βHgS > αHgS ratio has been obtained. In nitrate-containing solution vapor systems the inversion point can be positioned in 50 – 65°C temperature range, in which mixed phases, βHgS > αHgS are crystallising, after αHgS was formed betwen 25° – 50°C. In the case of nitrate-containing hydrothermal solutions the cinnabar and not the metacinnabar crystallises primarily below 50°C.

b) The As^{3+} ions in solution-vapor hydrothermal systems (at 25° – 100°C) prevent formation of αHgS, while in cases of presence of Sb^{3+} and Tl^{+} mono-phase βHgS has formed betwen 25° – 50°C, and βHgS > > αHgS polyphases at 75° – 100°C, similarly to the $HgCl_2 - H_2S$ system.

c) The experiments showed that the first crystallites, formed from solution-vapor systems, have always, βHgS structure initially, then in presence of nitrate ions, these rapidly (5 – 6 hours) alter to αHgS, wich is stabile below 60°C. In case of excess chloride-content, metacinnabar is formed below 50°C, above this temperature coexisting αHgS is also present. βHgS : αHgS ratio is 4 : 1.

d) Hg-depleted sulfide-phases are formed from solution-gas system, which become structurally ordered in solid-liquid (HgS + metal-containing solutions) systems. The *Hg*-deficiency is larger in phases of metacinnabar structure, the *Hg* : *S* ratios show greater differences then in phases of cinnabarstructure. In solid-phase – solution systems the *Hg* : *S* values are closer to the theoretical 1 : 1 ratio. This is most apparent for the cinnabar.

e) The recrystallisation of metacinnabar in solutions starts at room-temperature (30 days), through transitional mixed phases (αHgS > βHgS) with cinnabar dominance at 175°C and to final mono-phase system at 300°C.

f) In the $HgS_{(s)}$-$Na_2S_{(s)}$ system at 100°C mono-phase αHgS is produced. Its formation begins at room temperature.

g) The metacinnabar to cinnabar alterations in Na_2S are stimulated by the presence of antimony (Sb^{3+}) ions. The alteration begins at 125°C.

h) In $HgS_{(s)} - SbCl_{3(aq)}$ systems large (few millimeters in size) crystals have formed.

i) At our experimental conditions alteration of cinnabar to metacinnabar has *not* been recorded. In close system this alteration takes place at 344°C. At present there are no observations for alteration of cinnabar to metacinnabar during termometamorphosis.

j) In natural environment for the primary formation of metacinnabar chloridic hydrothermal solutions bave been proved to be the most favorable with As^{3+} content below 100°C, Tl^{+} content below 25°C, Sb^{3+} content below 50°C. The metacinnabar to cinnabar alteration may take place by

post-ore hydrothermal effects depending on temperature and ion-concentration of the solution, and possibly follows one of these schematic processes:

I. $HgS + H_2O$

a) 25°–150°C = βHgS > αHgS
b) 175°–250°C = αHgS > βHgS
c) 300°C = αHgS

II. $HgS + Na_2S + H_2O$

a) 25°– 50°C = βHgS > αHgS
b) 75°C = αHgS > βHgS
c) 100°–350°C = αHgS

III. $HgS + AsCl_3 + H_2O$

a) 25°–150°C = βHgS,
b) 175°C = βHgS > αHgS
c) 200°–250°C = αHgS > βHgS,
d) 300°C = αHgS

IV. $HgS + SbCl_3 + H_2O$

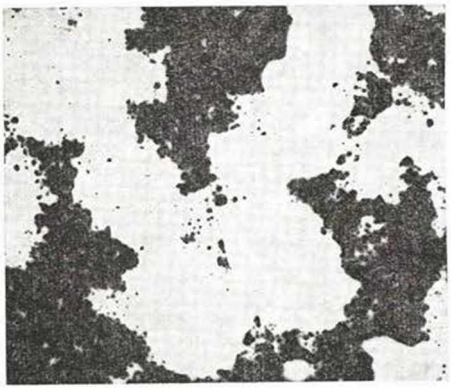
a) 25°–100°C = βHgS
b) 125°–150°C = βHgS > αHgS,
c) 175°–200°C = αHgS > βHgS
d) 250°–300°C = αHgS

V. $HgS + TlCl + H_2O$

a) 25°–125°C = βHgS,
b) 150°–200°C = βHgS > αHgS,
c) 250°C = αHgS > βHgS,
d) 300°–350°C = αHgS.

PLATE I

1



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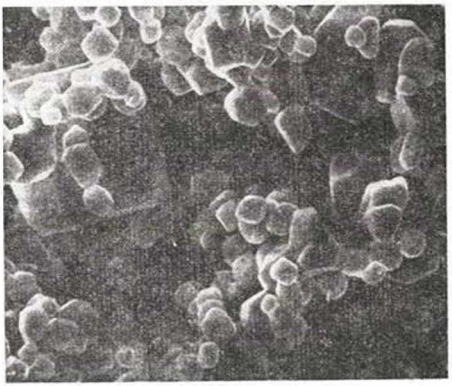
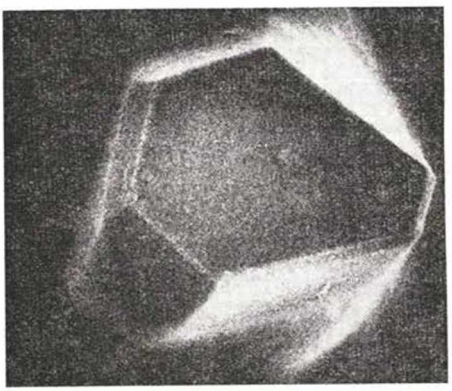
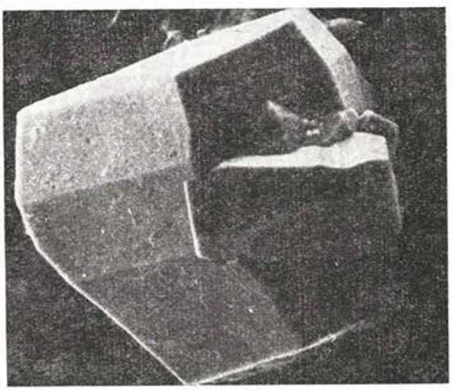






3

4

1 = $HgCl_2 + H_2O + H_2S - 50°C$
Aggregates of square-like crystal grains of Metacinnabar 120×.

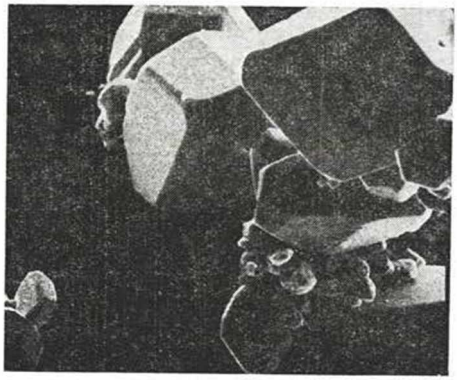
2 = *Metacinnabar* + $Na_2S + H_2O - 300°C$
Sub hexaedric, isometric grains of cinnabar with (0001) base plaines; 10,000x, electronicrograph.

3 = *Metacinnabar* + $As(III)Cl + H_2O - 250°C$.
Idiomorphic cinnabar with (0001), (h0kl), (0hkl), and (10$\bar{1}$0) forms; 20 000x. electronmicrograph.

4 = *Metacinnabar* + $As(III)Cl + H_2O - 300°C$
Idiomorphic cinnabar with different proto- and deutero rombohedra and base-planes; Twin-intergrowth. 3000 x; electronmicrograph.

PLATE 2

5



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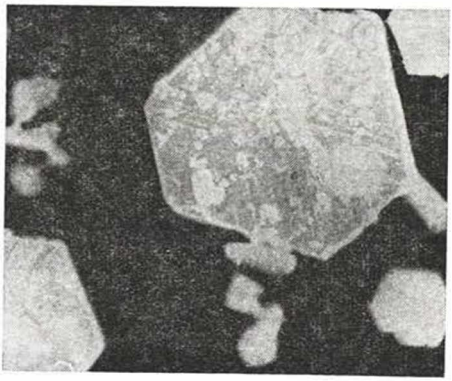

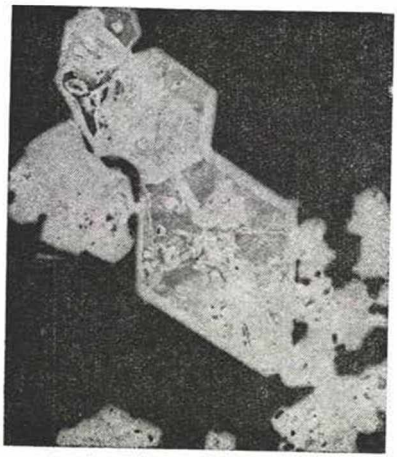

7

5 = *Metacinnabar + Sb(III)Cl + H_2O – 300°C.*
Idiomorphic cinnabar (0001), (1010) planes. 3000x; electronmicrograph.

6 = *Metacinnabar + Sb(III)Cl + H_2O – 250°C.*
Powder-preparatum. cinnabar crystals (=0,5 mm) with crystal-growth characteristics; 80 x.

7 = *Metacinnabar + Sb(III)Cl + H_2O – 300°C.*
Powder-praparatum. cinnabar crystals (=0,5 mm) with crystal-growth characteristics; 80 x.

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