

# New data on the composition of metacinnabar and Hg-sphalerite with an isomorphous Cd admixture

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## Abstract

The data on the composition of metacinnabar and Hg-sphalerite with an isomorphous Cd admixture from some mercury and complex ore objects are summarized. There are two varieties of metacinnabar: (1) cadmium-rich (9.25–15.80 wt.%), with the minimum quantity of Zn admixture (0.67–3.94 wt.%), which has the idealized formula (Hg,Cd,Zn)S (Ulandu) and (2) with increased amounts of Zn (2.21–10.83 wt.%) and Cd (6.00–14.10 wt.%), having the formula (Hg,Zn,Cd)S (Arzak, Kadyrel', Murzinskoe, Ravnou-1, Ravnou-2). The maximum content of isomorphous Cd (15.80 wt.%) was determined in the metacinnabar from the Ulandu ore occurrence. The Hg-sphalerites are compositionally divided into two groups: (1) with an increased Cd concentration (up to 7.96 wt.%) and (2) mainly with a low content of Cd admixture (0.0n–1.63 wt.%). The sphalerites of the first group are typical of mineral assemblages including Cd-Zn-enriched metacinnabar (Arzak, Kadyrel', Murzinskoe, Sarasa). The sphalerite of the Sarasa deposit is included into this group arbitrarily, because it contains more cadmium than the sphalerites of the second group, which are constituents of parageneses only with Zn-metacinnabar or lacking it (Nikitovka, Khaidarkan, Dzhizhikrut, Bayan-Khan, Aktash). There are some Hg-bearing varieties of sphalerite with the idealized formulas (Zn,Hg,Fe)S, (Zn,Hg,Cd)S, (Zn,Cd,Hg,Fe)S, (Zn,Fe,Cd,Hg)S, (Zn,Hg,Cd,Fe)S, (Zn,Fe,Hg,Cd)S, and (Zn,Hg,Cu)S, which transforms into (Zn,Cu,Hg)S. The maximum Cd admixture (7.96 wt.%) was established in Hg-sphalerite from the Kadyrel' ore occurrence. It is the highest content observed in natural Hg-bearing  $\beta$ -ZnS. The studied metacinnabar and sphalerite varieties are the only cubic phases of the natural system Zn–Hg–Cd–S, which is sometimes expanded because of minor admixtures of other metals. These varieties have a structure identical to the cubic phases of the synthetic systems Me–S and Me–Me–S, where Me = Zn, Cd, and Hg. None of Hg-bearing hexagonal solid solutions were found in the natural system Zn–Hg–Cd–S. The continuity of the natural isomorphous series  $\text{ZnS}_{\text{cub}}\text{--HgS}_{\text{cub}}$  has not been confirmed by finding of natural intermediate solid solutions at the series fragment between  $(\text{Zn}_{0.752}\text{Hg}_{0.248})\text{S}$  and  $(\text{Hg}_{0.539}\text{Zn}_{0.461})\text{S}$ . The metacinnabar varieties enriched in both Zn and Cd show no correlation between these elements. It is assumed that the host rocks with an increased content of cadmium compounds were the source of Cd for the formation of specific varieties  $\beta$ -HgS and  $\beta$ -ZnS.

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**Keywords:** Cd-bearing varieties; metacinnabar; Hg-sphalerite; system Zn–Hg–Cd–S

## Introduction

Black mercury sulfide ( $\beta$ -HgS) from the Redington mine (California, USA) was first described and called metacinnabar by Moore (1870). In the mineralogical reference books and special articles the presence of isomorphous admixtures of Zn, Se, Fe, and Mn in some specimens of this mineral was noted. Such specimens were named depending on the place of their findings as guadalcazarite (Zn = 4.23%, Se = 1.08%), onofrite (Se = 4.58–8.40%, Zn = 0.54–1.30%, Mn = 0.69%), and levigianite (Zn = 2.17%, Fe = 0.52%) (Bonstedt-Kupletskaya

and Chukhrov, 1960). Today these names are almost not used, and modification of  $\beta$ -HgS with Zn, Se, Fe or Mn admixtures is regarded as corresponding metacinnabar varieties. They are cubic phases of a mixed composition mainly of the isomorphous series ZnS (sphalerite)–HgS (metacinnabar) and HgS (metacinnabar)–HgSe (tiemannite).

The first information on new structural Cd admixture, dominating over the Zn admixture, in the black mercury sulfide was reported by Vasil'ev (1966). Chemical analyses of two bulk mineral samples from the Ulandu mercury occurrence (Gornyi Altai, Russia) yielded commensurate results for the contents of Cd (11.72–10.44 wt.%) and Zn (3.10–3.08 wt.%). The X-ray pattern of the mineral was the same as that of standard  $\beta$ -HgS. With the permission of the Commission on New Minerals of the All-Union Mineralogical

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Society, the author called this mineral “saukovite” in an honor of outstanding geochemist A.A. Saukov. The Commission on New Minerals of the International Mineralogical Association (IMA) considered it as a Zn-Cd variety of metacinnabar.

The next short paper on a similar mineral with higher Zn (9.5 wt.%) and lower Cd (6.0 wt.%) contents from the Tajikistan ore occurrence was published in 1975 (Bezuglyi, 1975). Then, metacinnabar with Zn and Cd admixtures was discovered at the Chauvai (Kyrgyzstan), Arzak deposits, and Kadyrel' mercury occurrence (Tuva, Russia), but data on it were published much later (Vasil'ev and Grechishcheva, 1997). Later on, black sulfide of a similar composition was found by N.K. Mortsev during the mineragraphic study of ores from the Murzinskoe gold deposit in Rudny Altai. Several fine grains of this mineral with main structural elements Hg, Cd, Zn, and S were observed as inclusions in cinnabar. Electron microprobe analysis determined a large amount of Cd and Zn in all grains, with the Cd content being the maximum (14.10 wt.%) of all detected earlier. The composition and optical properties permitted the mineral to be identified as Cd-Zn metacinnabar. Gas'kov et al. (2006) reported somewhat different composition and ranges of the content of main elements compared with the earlier data used in our paper.

Thus, there are six locations of hypogene metacinnabar with isomorphous admixtures of Cd and Zn (Table 1). All of them, except for the Murzinskoe deposit, belong to the mercury-ore formation. The mineral assemblages of these objects differ slightly in a set and amount of minerals. Among them, (Cd,Zn)-metacinnabar is most often found and sphalerite sporadically occurs; the latter, as a rule, crystallizes earlier than mercury sulfides—metacinnabar and cinnabar.

Isomorphous admixtures of Fe, Mn, Cd, and Cu in natural Hg-free  $\beta$ -ZnS have long been known. The mineral with any predominant admixture or the nearly pure one was called marmatite, cryshtophite, pržibramite, and cleiophane (Dana et al., 1944–1962; Doelter and Leitmeier, 1926). According to different sources, the maximum content of Cd admixture in pržibramite is either 2.47 wt.% (Bonshtedt-Kupletskaya and Chukhrov, 1960) or 5 wt.% (Betekhtin, 1950; Vlasov, 1964). In old chemical analyses of sphalerite, the Cd content varies from traces to 0.1 wt.% and, seldom, from 1.05 to 3.20 wt.% (Doelter and Leitmeier, 1926). Bur'yanova (1960) reported on pržibramite with 0.47–4.08 wt.% Cd. Sphalerite from the Kamyshlo deposit contained 1.00 to 3.50 wt.% Cd (Tsintsadze and Shvelashvili, 1960).

Table 1. Chemical composition of metacinnabar from some deposits (wt.%)

Analysis	Hg	Zn	Cd	Fe	Mn	S	Se	Total	Formula	Ore occurrence, deposit	Reference
1 (average)	68.87	3.09	11.08	–	–	15.61	–	98.65	(Hg <sub>0.70</sub> Cd <sub>0.20</sub> Zn <sub>0.10</sub> ) <sub>1.00</sub> S <sub>1.00</sub>	Ulandu	Vasil'ev (1966)
2	79.05	4.80	1.07	–	–	15.51	–	100.43	(Hg <sub>0.820</sub> Zn <sub>0.153</sub> Cd <sub>0.020</sub> ) <sub>0.993</sub> S <sub>1.007</sub>	Chauvai	Unpublished Vasil'ev's data
3	79.30	4.46	0.75	–	–	15.29	–	99.80	(Hg <sub>0.835</sub> Zn <sub>0.144</sub> Cd <sub>0.014</sub> ) <sub>0.993</sub> S <sub>1.007</sub>		
4	78.95	4.31	1.27	–	–	15.29	–	99.82	(Hg <sub>0.831</sub> Zn <sub>0.139</sub> Cd <sub>0.024</sub> ) <sub>0.994</sub> S <sub>1.006</sub>		
5 (average)	79.10	4.52	1.03	–	–	15.36	–	100.01	(Hg <sub>0.829</sub> Zn <sub>0.145</sub> Cd <sub>0.019</sub> ) <sub>0.993</sub> S <sub>1.007</sub>		
6 (average over four grains)	75.00	2.21	7.24	0.22	0.09	15.40	N.d.	100.16	(Hg <sub>0.781</sub> Zn <sub>0.134</sub> Cd <sub>0.071</sub> Fe <sub>0.008</sub> Mn <sub>0.003</sub> ) <sub>0.997</sub> S <sub>1.003</sub>	Arzak	The same
7 (average over four grains)	67.90	5.37	8.73	0.26	–	16.90	N.d.	99.16	(Hg <sub>0.657</sub> Zn <sub>0.160</sub> Cd <sub>0.151</sub> Fe <sub>0.009</sub> ) <sub>0.977</sub> S <sub>1.023</sub>	Kadyrel'	The same
8	67.36	9.50	6.00	?	?	17.14	?	100.00	(Hg <sub>0.628</sub> Zn <sub>0.272</sub> Cd <sub>0.100</sub> ) <sub>1.000</sub> S <sub>1.000</sub> (calculated from the contents of Zn and Cd)	Ravnou-1, 2	Bezuglyi (1975)
9	56.43	10.35	13.98	–	–	17.80	0.26	98.82	(Hg <sub>0.501</sub> Zn <sub>0.282</sub> Cd <sub>0.222</sub> ) <sub>1.005</sub> (S <sub>0.989</sub> Se <sub>0.006</sub> ) <sub>0.995</sub>	Murzinskoe	–
10	56.47	10.70	14.10	–	–	18.19	0.27	99.73	(Hg <sub>0.493</sub> Zn <sub>0.287</sub> Cd <sub>0.220</sub> ) <sub>1.000</sub> (S <sub>0.994</sub> Se <sub>0.006</sub> ) <sub>1.000</sub>		
11	56.25	10.83	14.10	–	–	18.30	0.19	99.67	(Hg <sub>0.490</sub> Zn <sub>0.290</sub> Cd <sub>0.219</sub> ) <sub>0.999</sub> (S <sub>0.997</sub> Se <sub>0.004</sub> ) <sub>1.001</sub>		
12	56.42	10.24	13.74	–	–	18.04	0.30	98.74	(Hg <sub>0.499</sub> Zn <sub>0.278</sub> Cd <sub>0.217</sub> ) <sub>0.994</sub> (S <sub>0.999</sub> Se <sub>0.007</sub> ) <sub>1.006</sub>		
13	55.47	10.51	13.35	–	–	18.36	0.24	98.43	(Hg <sub>0.492</sub> Zn <sub>0.284</sub> Cd <sub>0.209</sub> ) <sub>0.985</sub> (S <sub>1.010</sub> Se <sub>0.005</sub> ) <sub>1.015</sub>		
14 (average)	56.31	10.53	13.85	–	–	18.14	0.25	99.08	(Hg <sub>0.495</sub> Zn <sub>0.284</sub> Cd <sub>0.217</sub> ) <sub>0.996</sub> (S <sub>0.998</sub> Se <sub>0.005</sub> ) <sub>1.004</sub>		

Note. 1, 8, chemical analyses; 2–7, 9–14, microprobe analyses: 2–7—analyses on a JXA-5A microprobe, 9–14—analyses on a Camebax-Micro microprobe. N.d., not determined.

In the late 1960–70s, the first Hg-enriched (up to 35–38 wt.% Hg) sphalerites (some of them with a significant Cd admixture) were found in cinnabar ores (Gruzdev, 1975; Kuznetsov et al., 1978; Ozerova and Gruzdev, 1975; Vasil'ev and Lavrent'ev, 1969, 1976). In 1985–95, (Cd, Hg)- and Hg-sphalerites were discovered in the mercury ores and ores of complex Hg-bearing (including polymetallic and gold) deposits in other regions (Barbanson et al., 1985; Dini et al., 1995; Harris, 1989).

The presence of extraordinary metacinnabar variety at the Murzinskoe deposit gave rise to an electron-microprobe study of the composition of its precursor from the Ulandu mercury occurrence (Vasil'ev, 1966). The earlier chemical analyses of composite samples, often being a mixture of grains of different compositions, yielded the average contents of their components. Moreover, the minimum and maximum contents of elements and their distribution and correlation in the mineral remained unknown, but these parameters are required for the detailed characterization of any mineral and the differentiation of its species in possible isomorphous series.

Since Cd-rich Hg-sphalerite was found together with the new variety of mercury sulfide (Vasil'ev and Grechishcheva, 1997), it was necessary to verify its presence in mineral assemblages without Cd-metacinnabar from other objects in order to establish some conformity of its appearance and coexistence of both Cd-bearing varieties. For this purpose the composition of sphalerite from the Nikitovka (Ukraine), Khaidarkan (Kyrgyzstan), Dzshzhikrut (Tajikistan), and Ak-tash (Russia) mercury deposits and the complex Bayan-Khan deposit (Mongolia) was studied.

The composition of both minerals was determined on JXA-5A, MS-46, Camebax-Micro, and JEOL 8100 microprobes (accelerating voltage 20 kV, current 20 nA). Synthetic HgS ( $HgM_{\alpha}$ ,  $SK_{\alpha}$ ), HgSe ( $SeK_{\alpha}$ ), ZnS ( $ZnK_{\alpha}$ ), CdS ( $CdL_{\alpha}$ ) and  $CuFeS_2$  ( $CuK_{\alpha}$ ,  $FeK_{\alpha}$ ) were used as standards.

### The chemical composition of metacinnabar with isomorphous Cd and Zn admixtures

Using the results of analyses of metacinnabar from the Murzinskoe deposit, its formulas were calculated (Table 1), which show nearly the same contents of Zn + Cd atoms and Hg atoms (1:1). In percentage, Zn + Cd atoms amount to 49.8–50.9% (on average, 50.3%), with the portion of Cd atoms (21.2–22.0%) being lower than the portion of Zn atoms (28.5%). This proportion of atoms of the main component (Hg) and the sum of admixtures (Zn + Cd) suggests the formation of new mineral species of cubic symmetry in the natural system Zn–Hg–Cd–S. But, probably, it is the only example of crystallization of such metacinnabar. Similar varieties from other deposits usually contain <30% (Zn + Cd) atoms (see Table 1).

Among the new 85 “saukovite” grains from the Ulandu occurrence there are no individuals with the same concentration and proportion of main admixtures and mercury as in the metacinnabar from the Murzinskoe deposit. The contents of

elements vary in the following ranges (wt.%): Hg = 66.85–71.58, Cd = 9.25–15.80, Zn = 0.67–3.97, S = 15.00–16.58; Fe and Se were not detected (the sensitivity of the microprobe method was (wt.%): Hg = 0.09, Cd = 0.03, Zn = 0.04, Fe = 0.02, S = 0.02, Se = 0.07). More than 85% grains of the mineral have a high content of Cd: 11.03–13.99 wt.% in 30 grains and 14.00–15.80 wt.% in 43 grains, but the amount of Zn in these grains is very low (0.67–1.63 wt.%). More Zn admixture (2.29–3.97 wt.%) was detected only in 12 specimens having a Cd concentration of 9.25–10.93 wt.%. Obviously, the data of the wet chemical analysis would be different from the previously published ones (Vasil'ev, 1966) if all these grains were combined into a common preparation. Table 2 presents the typical analyses with the minimum, increased, and the highest Cd contents.

The analyzed metacinnabar grains from the Ulandu occurrence have different compositions and show a relatively even distribution of elements, a minor variation in their contents, and an inverse correlation of Cd and Zn with Hg.

### The chemical composition of sphalerite with isomorphous Hg and Cd admixtures

The earlier and new data on the composition of sphalerite are presented in Table 3. Two groups of natural  $\beta$ -ZnS are distinguished by Cd concentration: (1) with medium and increased contents of Cd admixture and (2) mainly with a low content of this element. Sphalerite from the Arzak deposit and Kadyrel' ore occurrence (Tuva) and, partly, the Sarasa deposit (Gornyi Altai) are in the first group. The sphalerite varieties of the second group are typical of the rest deposits.

In the paragenesis of the polysulfide stage of ore deposition at the Arzak deposit (Grechishchev et al., 1978) sphalerite occurs in different combinations with accompanying sulfides and sulfosalts. Besides (Cd,Hg)- and (Hg,Cd)-sphalerites, there are two other mineral varieties: (Fe,Cd)-sphalerite with the minimum Hg admixture (0.54–0.99 wt.%) and (Fe,Cd)-sphalerite with scarce Cd admixture (Table 3, No. 7). This diversity of the mineral varieties produced at the same stage might indicate the variable parameters of their formation process, including a temporal change in the contents of the producing-medium components.

The maximum content of Cd admixture (up to 7.96 wt.%) was determined in Hg-sphalerite from the Kadyrel' mercury occurrence. The limiting contents of elements and the composition of some Cd-enriched grains are given in Table 3 (No. 8). However, no distinct correlation between the contents of Cd and Hg is observed, because there are varieties with Hg:Cd (at.) 1:1. They have the empirical formulas

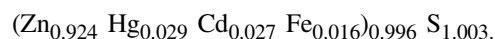
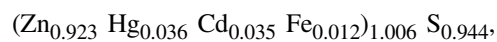


Table 2. Composition of metacinnabar from the Ulandu ore occurrence (Gornyi Altai) in the sequence of increase in the average Cd content (wt.%)

Grain no.	Hg	Cd	Zn	S	Total	Formula
24 (2)	<u>70.25</u> 70.09–70.41	<u>9.44</u> 9.25–9.63	<u>3.95</u> 3.92–3.97	<u>15.86</u> 15.75–15.96	99.50	(Hg <sub>0.708</sub> Cd <sub>0.170</sub> Zn <sub>0.122</sub> ) <sub>1.000</sub> S <sub>1.000</sub>
27 (4)	<u>70.76</u> 69.65–71.52	<u>9.52</u> 9.40–9.70	<u>3.73</u> 3.60–3.82	<u>15.89</u> 15.34–16.30	99.90	(Hg <sub>0.713</sub> Cd <sub>0.171</sub> Zn <sub>0.115</sub> ) <sub>0.999</sub> S <sub>1.001</sub>
6 (2)	<u>70.25</u> 69.96–70.54	<u>10.57</u> 10.20–10.93	<u>2.93</u> 2.92–2.93	<u>15.81</u> 15.70–15.92	99.56	(Hg <sub>0.713</sub> Cd <sub>0.191</sub> Zn <sub>0.091</sub> ) <sub>0.995</sub> S <sub>1.004</sub>
53 (2)	<u>69.39</u> 69.12–69.65	<u>11.23</u> 10.86–11.60	<u>3.03</u> 3.02–3.03	<u>15.88</u> 15.81–15.94	99.53	(Hg <sub>0.701</sub> Cd <sub>0.202</sub> Zn <sub>0.094</sub> ) <sub>0.997</sub> S <sub>1.003</sub>
9 (4)	<u>69.75</u> 68.92–70.75	<u>11.33</u> 11.03–11.60	<u>2.78</u> 2.32–3.38	<u>15.85</u> 15.62–16.06	99.71	(Hg <sub>0.706</sub> Cd <sub>0.206</sub> Zn <sub>0.086</sub> ) <sub>0.998</sub> S <sub>1.003</sub>
4 (3)	<u>70.07</u> 69.98–70.20	<u>11.41</u> 11.33–11.49	<u>2.99</u> 2.94–3.07	<u>16.02</u> 15.81–16.33	100.49	(Hg <sub>0.702</sub> Cd <sub>0.204</sub> Zn <sub>0.092</sub> ) <sub>0.998</sub> S <sub>1.002</sub>
1 (2)	<u>69.95</u> 69.80–70.10	<u>11.47</u> 11.14–11.79	<u>2.80</u> 2.75–2.84	<u>15.86</u> 15.57–16.14	100.08	(Hg <sub>0.706</sub> Cd <sub>0.206</sub> Zn <sub>0.087</sub> ) <sub>0.999</sub> S <sub>1.001</sub>
61 (3)	<u>68.80</u> 68.56–69.13	<u>13.69</u> 13.62–13.80	<u>1.47</u> 1.44–1.51	<u>15.66</u> 15.49–15.82	99.62	(Hg <sub>0.703</sub> Cd <sub>0.250</sub> Zn <sub>0.046</sub> ) <sub>0.999</sub> S <sub>1.001</sub>
72 (3)	<u>68.03</u> 67.95–68.17	<u>14.01</u> 13.95–14.11	<u>1.39</u> 1.35–1.42	<u>15.52</u> 15.39–15.59	98.95	(Hg <sub>0.700</sub> Cd <sub>0.257</sub> Zn <sub>0.044</sub> ) <sub>1.001</sub> S <sub>0.999</sub>
8 (2)	<u>68.87</u> 68.52–69.22	<u>14.20</u> 14.00–14.40	<u>0.96</u> 0.95–0.97	<u>15.72</u> 15.64–15.79	99.75	(Hg <sub>0.705</sub> Cd <sub>0.259</sub> Zn <sub>0.030</sub> ) <sub>0.994</sub> S <sub>1.006</sub>
78 (3)	<u>67.66</u> 67.02–67.11	<u>14.70</u> 14.63–14.81	<u>1.48</u> 1.45–1.54	<u>15.77</u> 15.62–15.92	99.50	(Hg <sub>0.686</sub> Cd <sub>0.266</sub> Zn <sub>0.046</sub> ) <sub>0.998</sub> S <sub>1.002</sub>
48 (3)	<u>67.96</u> 67.51–68.62	<u>14.70</u> 14.57–14.81	<u>0.83</u> 0.72–0.92	<u>15.68</u> 15.50–15.91	99.17	(Hg <sub>0.698</sub> Cd <sub>0.269</sub> Zn <sub>0.026</sub> ) <sub>0.993</sub> S <sub>1.007</sub>
43 (4)	<u>67.53</u> 67.22–67.90	<u>15.22</u> 15.07–15.37	<u>0.74</u> 0.70–0.77	<u>15.78</u> 15.65–15.91	99.27	(Hg <sub>0.690</sub> Cd <sub>0.278</sub> Zn <sub>0.023</sub> ) <sub>0.991</sub> S <sub>1.009</sub>
67 (3)	<u>67.68</u> 67.25–68.10	<u>15.32</u> 15.23–15.38	<u>0.78</u> 0.76–0.80	<u>15.70</u> 15.70–15.71	99.48	(Hg <sub>0.692</sub> Cd <sub>0.280</sub> Zn <sub>0.024</sub> ) <sub>0.996</sub> S <sub>1.004</sub>
57 (2)	<u>67.07</u> 67.02–67.11	<u>15.64</u> 15.47–15.80	<u>0.86</u> 0.85–0.86	<u>15.57</u> 15.44–15.69	99.14	(Hg <sub>0.688</sub> Cd <sub>0.286</sub> Zn <sub>0.027</sub> ) <sub>1.001</sub> S <sub>0.999</sub>

Note. Parenthesized is the number of determination. Average contents are above the line, and the range of contents is below the line. Analyses were carried out on a JEOL 8100 microprobe (analyst E.N. Nigmatulina, Institute of Geology and Mineralogy, Novosibirsk).

The second group of sphalerite varieties is characterized by a wide variation in the contents of Hg admixture in the zonal grains and a negligible content of Cd admixture (the latter is specific for most of Hg-free sphalerites at deposits of different genetic types). The calculated formulas of the varieties (Table 3, Nos. 1–5) show the changed positions of isomorphous elements Hg, Cd, Fe, and Cu depending on which element is predominant. These changes are responsible for the appearance of new mineral varieties: (Cd,Hg)-, (Cd,Fe)-, (Hg,Fe)-, and almost Cd-free (Cu,Hg)-sphalerites. The latter variety (lacking Fe and Cd) has the idealized formula (Zn,Hg,Cu)S (Table 3, No. 5), which transforms into (Zn,Cu,Hg)S for eight of twenty-one analyses, where copper prevails.

The study of sphalerite from different deposits (Table 3) showed that the first-group varieties, coexisting with (Cd,Zn)-metacinnabar in the paragenesis, are the most Cd-enriched, and the second-group varieties are not accompanied by any hypogene compounds with Cd.

## Discussion

The literature and our data evidence the presence of new metacinnabar and sphalerite varieties with the idealized formulas (Hg,Zn,Cd)S–(Hg,Cd,Zn)S, (Zn,Hg,Cd)S–(Zn,Cd,Hg)S, (Zn,Hg,Cd,Fe)S–(Zn,Cd,Hg,Fe)S, (Zn,Fe,Cd,Hg)S–(Zn,Fe,Hg,Cd)S, and (Zn,Hg,Cu)S–(Zn,Cu,Hg)S in parageneses of some mercury and complex deposits. All the varieties are complex isomorphous mixtures of the natural system Zn–Hg–Cd–S and, more seldom, the system Zn–Hg–Cd–Fe–S. The composition of these mixtures is formed with the participation of the binary compounds of the systems Me–S: Zn–S, Cd–S, Hg–S, etc., in which, according to experimental results, several polymorphous phases often coexist.

For example, the system Zn–S includes eight phases: hexagonal polytypes ZnS–2H, ZnS–4H, ZnS–6H, ZnS–8H, and ZnS–10H, trigonal phases ZnS–3R and ZnS–15R, and cubic compound  $\beta$ -ZnS. The latter exists in nature mainly as sphalerite. Modifications ZnS–2H (wurtzite) and ZnS–3R (matraite) are scarcer, and other hexagonal polytypes are

Table 3. Composition of Hg-bearing sphalerites from some mercury and complex objects (wt.%)

No.	Deposit, ore occurrence	Zn	Hg	Cd	Fe	Additional admixture	Formula
1	Nikitovka (11)	45.54–51.15	18.62–26.04	0.04–0.11	0.91–1.24	–	(Zn <sub>0.848</sub> Hg <sub>0.137</sub> Fe <sub>0.024</sub> Cd <sub>&lt;0.001</sub> )1.010S <sub>0.990</sub>
2	Khaidarkan (12)	50.27–59.35	7.97–19.24	0.57–1.10	Not found	Cu 0.03–0.20	(Zn <sub>0.920</sub> Hg <sub>0.065</sub> Cd <sub>0.007</sub> Cu <sub>0.001</sub> )0.993S <sub>1.007</sub>
3	Dzhirzhikrut (6)	44.59–65.50	1.38–30.05	0.18–1.63	0.06–0.25	–	(Zn <sub>0.918</sub> Hg <sub>0.084</sub> Cd <sub>0.006</sub> Fe <sub>0.003</sub> )1.011S <sub>0.989</sub>
4	Bayan-Khan (11)	54.76–65.58	1.93–16.09	0.20–0.24	Below detection limit	Mn 0.04	(Zn <sub>0.968</sub> Hg <sub>0.031</sub> Cd <sub>0.002</sub> )1.001S <sub>0.998</sub>
5	Aktash (21)	46.57–60.37	5.64–16.92	0.02–0.20	0.00–0.28	Cu 1.35–8.51	(Zn <sub>0.887</sub> Hg <sub>0.060</sub> Cu <sub>0.060</sub> Fe <sub>0.001</sub> Cd <sub>&lt;0.001</sub> )1.009S <sub>0.991</sub>
6	Sarasa (7)*	57.13–62.35	3.96–11.05	1.96–2.52	0.22–0.32	–	(Zn <sub>0.937</sub> Hg <sub>0.046</sub> Cd <sub>0.021</sub> Fe <sub>0.006</sub> )1.010S <sub>0.990</sub>
7	Artak (4)*	62.0–62.8	1.05–1.45	3.03–3.98	0.26	Mn 0.04	(Zn <sub>0.956</sub> Cd <sub>0.031</sub> Hg <sub>0.007</sub> Fe <sub>0.005</sub> Mn <sub>0.001</sub> )1.000S <sub>1.000</sub>
	(33)	62.50–64.02	0.54–0.99	1.44–2.66	1.21–1.89	–	(Zn <sub>0.955</sub> Fe <sub>0.028</sub> Cd <sub>0.016</sub> Hg <sub>0.004</sub> )1.003S <sub>0.997</sub>
	(12)	59.55–61.63	1.77–4.15	0.44–0.94	1.99–3.78	–	(Zn <sub>0.930</sub> Fe <sub>0.051</sub> Hg <sub>0.014</sub> Cd <sub>0.006</sub> )1.001S <sub>0.999</sub>
8	Kadyrel' (60)*	48.45–59.03	5.62–18.38	2.33–7.96	0.17–1.59	–	(Zn <sub>0.88</sub> Hg <sub>0.07</sub> Cd <sub>0.04</sub> Fe <sub>0.01</sub> )1.00S <sub>0.99</sub>
	(5)	49.66–50.16	16.30–18.38	4.05–5.14	0.21–0.39	–	(Zn <sub>0.859</sub> Hg <sub>0.096</sub> Cd <sub>0.046</sub> Fe <sub>0.006</sub> )1.007S <sub>0.993</sub>
	(4)	48.45–51.41	14.59–15.96	4.50–5.40	0.38–0.66	–	(Zn <sub>0.856</sub> Hg <sub>0.086</sub> Cd <sub>0.049</sub> Fe <sub>0.010</sub> )1.001S <sub>0.999</sub>
	(4)	48.85–52.00	11.25–16.99	5.61–7.18	0.41–0.62	–	(Zn <sub>0.859</sub> Hg <sub>0.076</sub> Cd <sub>0.066</sub> Fe <sub>0.010</sub> )1.011S <sub>0.989</sub>
	(2)	51.09–51.11	10.81–11.01	7.80–7.96	0.60–0.61	–	(Zn <sub>0.858</sub> Cd <sub>0.077</sub> Hg <sub>0.060</sub> Fe <sub>0.011</sub> )1.006S <sub>0.994</sub>
	(1)	58.17	6.44	4.46	0.62	–	(Zn <sub>0.919</sub> Cd <sub>0.041</sub> Hg <sub>0.033</sub> Fe <sub>0.012</sub> )1.005S <sub>0.995</sub>
	(1)	54.24	9.09	5.56	0.78	–	(Zn <sub>0.887</sub> Cd <sub>0.053</sub> Hg <sub>0.048</sub> Fe <sub>0.015</sub> )1.003S <sub>0.996</sub>

Note. Parenthesized is the number of analyses; the formulas were calculated from the average compositions. Analyses were carried out on MS-46 and Camebax-Micro microprobes (analysts Yu.G. Lavrent'ev and L.V. Usova, Institute of Geology and Mineralogy, Novosibirsk).

\* Analyses were borrowed from Grechishchev et al. (1978), Vasil'ev and Lavrent'ev (1976), and Vasil'ev and Grechishcheva (1997).

extremely rare (Betekhtin, 1950; Bonshtedt-Kupletskaya and Chukhrov, 1960; Buck and Strock, 1955; Dana et al., 1944–1962; Frondel and Palache, 1950; Koch, 1958; Nickel and Nichols, 1991; Strunz and Nickel, 2001).

Two CdS compounds exist in the system Cd–S: hexagonal phase with wurtzite structure and cubic phase with the sphalerite crystal lattice (Ulrich and Zachariasen, 1925). Their natural analogs are greenockite and rarer hawleyite.

At least three phases were synthesized in the system Hg–S:  $\alpha$ -HgS (trigonal) with an individual crystal structure,  $\beta$ -HgS (cubic) with the sphalerite lattice, and  $\gamma$ -HgS (hexagonal, of wurtzite structure?)<sup>1</sup>. In structure they correspond to cinnabar, metacinnabar, and hypercinnabar, respectively (Allen et al., 1912; Auvray and Genet, 1973; Mikolaichuk and Dutchak, 1965; Potter and Barnes, 1978; Protod'yakonova et al., 1971; Rittner and Schulman, 1943; Strunz and Nickel, 2001).

Each of the above systems has isostructural phases, which favors the formation of continuous or limited series of solid solutions ZnS–CdS, ZnS–HgS, and CdS–HgS in the ternary systems Zn–Cd–S, Zn–Hg–S, and Cd–Hg–S, since the ionic and atomic radii of the cations are commensurate. Experiments in these systems were carried out in different time and under different conditions, which explains the difference in the results obtained (Charbonnier and Murat, 1974; Cherin et al., 1970; Kremheller et al., 1960; Moltzau and Kolthoff, 1936;

Rittner and Schulman, 1943; Tauson and Abramovich, 1980; Wachtel, 1960).

Solid solutions of the series ZnS–CdS were obtained in the ternary system Zn–Cd–S (as in the binary systems Zn–S and Cd–S earlier). They are of two syngonies: cubic, with the sphalerite crystal lattice, and hexagonal, with the wurtzite lattice (Ballentine and Ray, 1961; Charbonnier and Murat, 1974; Cherin et al., 1970; Hurlbut, 1957). The cubic phases correspond to Hg-free prĭzbramites with an isomorphic Cd admixture (up to 5%), and the hexagonal ones, to Cd-wurtzite and Zn-greenockite, (Zn<sub>0.590</sub>Cd<sub>0.423</sub>)1.013S<sub>0.987</sub> and (Cd<sub>0.561</sub>Zn<sub>0.475</sub>)1.036S<sub>0.964</sub>, respectively (Hurlbut, 1957).

Under the experimental conditions, the isomorphous series ZnS–HgS of the system Zn–Hg–S is continuous, at least up to 80 mol.% HgS, and includes phases of varying composition of one solid solution with a cubic symmetry, with the lattice parameter increasing together with the content of HgS admixture in ZnS (Charbonnier and Murat, 1974; Kremheller et al., 1960; Wachtel, 1960). In this case, the middle member of the series, (Zn<sub>0.5</sub>Hg<sub>0.5</sub>)S, must have the following composition (wt.%): Zn = 19.80, Hg = 60.77, S = 19.43.

The ores of mercury and mercury-bearing deposits contain many varieties of sphalerite and metacinnabar with different contents of Hg in the former and Zn in the latter. The nonzonal crystals of sphalerite with the limiting content of Hg (38 wt.%) (Gruzdev, 1975)<sup>2</sup> and composition reduced to 100% (Zn = 37.58, Hg = 37.98, S = 24.48 wt.%) correspond to the formula

<sup>1</sup> This phase, specified as  $\beta'$ -HgS, was first discovered among the synthesis products by Allen et al. (1912).

<sup>2</sup> The total compositions of minerals are not given.

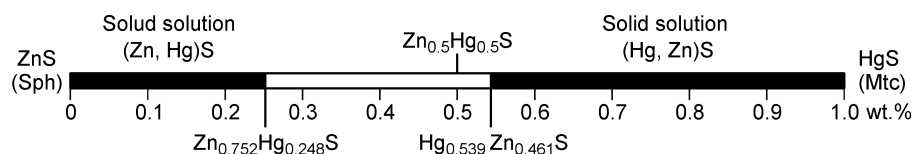


Fig. 1. The bounds of the coexistence of Hg-sphalerite (Sph) and Zn-metacinnabar (Mtc) solid solutions in the natural series ZnS–HgS.

( $\text{Zn}_{0.752}\text{Hg}_{0.248}$ ) $_{1.000}\text{S}_{1.000}$ . Later, varying contents of Hg (12.49–45.53 wt.%) were determined in the zonal crystals (Dini et al., 1995), but they are lower by 15 wt.% than those necessary for the middle member of the series. Zonal sphalerite has the formula ( $\text{Zn}_{0.501}\text{Hg}_{0.307}\text{Fe}_{0.124}\text{O}_{0.932}\text{S}_{1.064}\text{Se}_{0.03}$ ) $_{1.067}$ . The formula of the Zn-richest (17.7 wt.%) metacinnabar (Leonard et al., 1978)<sup>3</sup> ( $\text{Hg}_{0.539}\text{Zn}_{0.461}$ ) $_{1.000}\text{S}_{1.000}$  was tentatively determined from the calculated composition (wt.%): Hg = 63.47, Zn = 17.70, S = 18.82. Ignoring the rest isomorphous admixtures in both minerals, the compositions of Hg and Zn admixtures in the series ZnS–HgS (with the maximum contents of Hg in nonzonal sphalerite and Zn in metacinnabar) show the absence of solid solutions, including the middle member ( $\text{Hg}_{0.5}\text{Zn}_{0.5}$ ) $_{1.0}\text{S}_{1.0}$  (Fig. 1). This fact as well as the conclusion about the rupture of miscibility in the above series (Tauson and Abramovich, 1980; Urusov, 1978, 1987) and the finding of probably metastable tetragonal sulfide—polhemusite ( $\text{Zn,Hg}$ )S, a polymorph of Hg-sphalerite (Leonard et al., 1978), intruding into its stability field,—suggest that the natural series ZnS–HgS has a different structure.

As in the system Zn–Cd–S, mixed crystals of wurtzite and sphalerite structures were synthesized in the system Cd–Hg–S, and the discontinuous structure of the series CdS–HgS was established (Charbonnier and Murat, 1974; Kremheller et al., 1960; Rittner and Schulman, 1943). According to Kremheller et al. (1960), the series is subdivided into three intervals with solid solutions and their mechanical mixtures with different contents of HgS admixtures. At the first segment from the side of CdS, all phases ( $\text{Cd,Hg}$ )S with HgS = 0–43 mol.% (Hg = 47.29 and Cd = 35.13 wt.%) are of wurtzite structure and have the same(?) parameters of the hexagonal unit cell:  $a = 4.13 \text{ \AA}$ ,  $c = 6.74 \text{ \AA}$ .

The second interval with HgS = 43–60 mol.% in the synthesis products (Hg = 47.29–60.98 and Cd = 35.13–22.78 wt.%) is a mechanical mixture of hexagonal and cubic solid solutions with the wurtzite and sphalerite crystal lattices. Unfortunately, the exact compositions of both types of solutions are not known. The third interval with HgS > 60 mol.% includes solid solutions ( $\text{Hg,Cd}$ )S of the sphalerite structure with the constant(?) parameter  $a$  of the unit cell,  $5.83 \text{ \AA}$ . This conclusion was drawn because of the insufficiently precise data of X-ray analysis, which showed that the parameter  $a$  of the cubic structures in the series decreases as the CdS content increases, at least to 30 mol.%, when all substance is still homogeneous (Rittner and Schulman, 1943). The data reported by Kremheller et al. (1960) show that the maximum saturation

of hexagonal ( $\text{Cd}_{0.57}\text{Hg}_{0.43}$ )S crystals with mercury and cubic ( $\text{Hg}_{0.60}\text{Cd}_{0.40}$ )S crystals with cadmium is limited by 47.29 wt.% Hg and 22.78 wt.% Cd. But it is not ruled out that these values are not limiting, since the compositions of phases from the region of their coexistence are not known.

Charbonnier and Murat (1974), who also studied the system Cd–Hg–S, subdivided the series CdS–HgS into five segments with solid solutions of hexagonal and cubic symmetry and mechanical mixtures of binary compounds  $\text{CdS}_{\text{hex}} + \text{HgS}_{\text{cub}}$  and  $\text{HgS}_{\text{cub}} + \text{HgS}_{\text{hex}}$ . The hexagonal members of the series are localized at two segments restricted by the compositions from pure  $\text{CdS}_{\text{hex}}$  to  $\text{Hg}_{0.55}\text{Cd}_{0.45}\text{S}$  (Hg = 57.17 and Cd = 26.21 wt.%) and from  $\text{Hg}_{0.95}\text{Cd}_{0.05}\text{S}$  (Hg = 83.49 and Cd = 2.46 wt.%) to  $\text{HgS}_{\text{hex}}$ . The cubic phases lie between the isomorphous mixtures  $\text{Hg}_{0.67}\text{Cd}_{0.33}\text{S}$  (Hg = 66.03 and Cd = 18.22 wt.%) and  $\text{Hg}_{0.90}\text{Cd}_{0.10}\text{S}$  (Hg = 80.65 and Cd = 5.02 wt.%).

Comparison of the experimental results from the above publications shows a significant difference between the structures of the series CdS–HgS and between the Hg contents in the hexagonal crystals but close Cd contents in the cubic crystals. Nevertheless, there is a general regularity: The series intervals with hexagonal phases are longer, and the mixtures of compounds can incorporate much Hg without the crystal structure change. However, no natural hexagonal analogs ( $\text{Cd,Hg}$ )S, ( $\text{Hg,Cd}$ )S, ( $\text{Zn,Hg}$ )S, and ( $\text{Hg,Zn}$ )S (which might be considered Hg-greenockites, wurtzites, and new minerals) have been found yet for the hexagonal solid solutions of the experimental systems Cd–Hg–S and Zn–Hg–S.

Experimental data on the system Zn–Hg–Cd–S are minor. Four-component cubic luminophores ( $\text{Zn,Cd,Hg}$ )S similar in composition to some Hg–Cd-sphalerites were synthesized in this system (Wachtel, 1960). It is unclear whether any isomorphous mixtures similar to Cd-metacinnabar were obtained or not.

Metacinnabar of mercury deposits (Tables 1 and 2) contains 0.00 to 15.80 wt.% isomorphous Cd, whereas the synthesized phases ( $\text{Hg,Cd}$ )S are richer in it: 16.72, 18.22, and 22.78 wt.% (Charbonnier and Murat, 1974; Kremheller et al., 1960; Rittner and Schulman, 1943). The same peculiarity is observed in Hg-sphalerite accompanying metacinnabar: The maximum content of Cd in it is  $\approx 8$  wt.%, i.e., much lower than that in the synthetic phases (Wachtel, 1960). The difference in Cd content between the natural and synthetic mixed crystals is, most likely, due to the different physicochemical parameters of their formation processes. One of the main factors determining the isomorphous capacity and changes in the mixture composition is the temperature of the ambient medium. At mercury deposits, parageneses form with the participation of

<sup>3</sup> The total compositions of minerals are not given.

low-temperature ( $\leq 250$  °C) multielemental fluids, but most of the experiments were carried out at moderate and high temperatures (350–900 °C), high pressures, and high Cd contents in the system with a limited set of components. This probably explains why the synthetic solutions are richer in Cd.

There are no definite data on the source of Cd participating in the formation of specific metacinnabar and sphalerite varieties. It is not ruled out that Cd enters the mineral structure as a redeposited element borrowed by the ore-bearing solution from the surrounding rocks, its primary concentrators. This assumption is made, first of all, for the Cd-enriched varieties and is based on the studies by Bur'yanova (1960), who established the accumulation of authigenous Cd compounds (greenockite, cadmoselite, Cd-sphalerite) in the Devonian terrigenous deposits in Tuva during their early diagenesis. The above Cd-enriched varieties were found in the ores of objects localized in Ordovician and Devonian diagenetic sedimentary and volcanosedimentary rocks in Gornyi Altai (Ulandu, Sarasa) and Tuva (Arzak, Kadyrel'): sandstones and tuffstones enriched in Cd (according to spectral-analysis data). The enclosing rocks of the Chauvai and Murzinskoe deposits and the ore occurrences in Tajikistan might also be "infected" with Cd.

## Conclusions

1. The performed study has revealed two varieties of natural  $\beta$ -HgS: (Zn,Cd)- and (Cd,Zn)-metacinnabar with the idealized formulas (Hg,Cd,Zn)S and (Hg,Zn,Cd)S, respectively, and several varieties of Hg-sphalerite, with predominant isomorphous mixtures of Hg, Cd, Fe, and, more seldom, Cu.

2. The maximum contents of Cd (15.80 wt.%) have been determined in the metacinnabar from the Ulandu deposit in Gornyi Altai and in the Hg-sphalerite from the Kadyrel' mercury occurrence in Tuva.

3. Cadmium and zinc coexisting in the metacinnabar not always show correlation in contents.

4. The studied  $\beta$ -HgS and  $\beta$ -ZnS varieties are the only cubic derivatives of the natural system Zn–Hg–Cd–S, sometimes expanded because of the presence of secondary admixtures of other metals. In crystal structure they are similar to the binary compounds of cubic solid solutions of the experimental systems Me–S and Me–Me–S, where Me = Zn, Cd, and Hg. No natural Hg-bearing hexagonal solid solutions of the system Zn–Hg–Cd–S have been found yet.

5. Cadmium participating in the formation of Cd-enriched metacinnabar and Hg-sphalerite is assumed to come from a local source.

6. The complete isomorphous series  $\text{ZnS}_{\text{cub}}\text{--HgS}_{\text{cub}}$  is not known in nature, because intermediate solid solutions were not discovered at the long medium segment between  $(\text{Zn}_{0.752}\text{Hg}_{0.248})\text{S}$  and  $(\text{Hg}_{0.539}\text{Zn}_{0.461})\text{S}$ .

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