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GEOCHEMISTRY

Maikainite $Cu_{20}(Fe,Cu)_6Mo_2Ge_6S_{32}$ and Ovamboite $Cu_{20}(Fe,Cu,Zn)_6W_2Ge_6S_{32}$: New Minerals in Massive Sulfide Base Metal Ores

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In addition to molybdenite, tungstenite, and iordisite, complex sulfides of Mo and W (hemusite, kiddcreekite, castanite, Mo- and W-containing colusite, Ge-colusite, and germanite) have been detected in hydrothermal ores. The standard pink germanite contains traces of Mo and W, while the yellowish modification contains as much as 1–3% W and/or Mo [2–15]. In ores from massive sulfide base metal deposits (Tsumeb, Namibia; Maikain, Kazakhstan), researchers have found complex sulfides of Cu(Fe,Zn), Ge(As,Ga), and (Mo,W) [4, 12] associated with bornite, sphalerite, tennantite, germanite $Cu_{20}(Cu,Fe,Zn)_6Fe_2(Ge,As,Ga)_6Se_{32}$ [3], Ge-colusite $Cu_{20}(Cu,Fe,Zn)_6V_2(Ge,As)_6Se_{32}$ [5], renierite, Ge-mawsonite, Ge-briartite, sulvanite, and others. The Mo-dominated mineral was named maikainite after the locality of its first finding, whereas the W-dominated modification was named ovamboite after the Ovamboland region hosting the Tsumeb deposit (Namibia).[1]

Maikainite. In the Au-bearing massive sulfide base metal ore of the Maikain deposit, maikainite is found as tiny (up to 45 μm) oval particles and rare crystals (morphologically similar to octahedron or rhombododecahedron) scattered in sphalerite and bornite grains among barite aggregates. In the Ge-bearing massive sulfide base metal ore of the Tsumeb deposit, this mineral is observed as round segregations and emulsion dissemination, which are distinctly separated from germanite, and autonomous crystal overgrowths on Ge-colusite. Like molydoscheelite developed in the core of scheelite crystals, maikainite makes up the core of zonal crystals, while ovamboite is developed in the outer zone. The size of Tsumeb maikainite grains commonly varies from 3 to 40 μm (maximum 150 μm). In reflected light, the mineral color varies from bright yellow to grayish yellow. Its reflectivity is lower relative to tennantite but higher relative to sphalerite and germanite. The mineral is isotropic. Cleavage and internal reflections are absent. The relative relief is close to that of germanite. The VHN_{30} value ranges from 275 to 345 kg/mm^2 (average 305 kg/mm^2). Contents of Cu, Fe, Zn, and S are rather stable (Table 1). Element pairs Mo–W and Ge–As are characterized by negative correlations. However, (Mo + W) and (Ge + As) atomic contents are approximately constant. The maikainite formula fits $Cu_{20}(Fe,Cu,Zn)_6(Mo,W,V)_2(Ge,As,Ga)_6S_{32}$ in the generalized form and $Cu_{20}(Fe,Cu)_6Mo_2Ge_6S_{32}$ in the stoichiometric form. Its XRD pattern is close to that of germanite [13] and Ge-colusite [5]. Maximal reflections in the powder XRD image are as follows Å: 3.07 (10) (222), 1.884 (8) (440), and 1.603 (4) (622) (Table 2). The cubic lattice has the following parameters: a_0 = 10.64 (1) (Å), V = 1205 (3) $Å^3$, Z = 1, and X-ray density = 4.453 g/cm^3. Reflection spectra are characterized by complex patterns with a low-angle maximum in the yellow region (Table 3).

Ovamboite. This mineral is observed as distinct round segregations and emulsion dissemination in germanite aggregates and as outer zones of maikainite crystal overgrowths on Ge-colusite. Ovamboite is usually developed in specific sectors where germanite is actively replaced by Zn-tennantite. Germanite associated with ovamboite contains hallite decomposition lamellae, whereas hallite ingrowths are absent in ovamboite. The size of ovamboite grains ranges from 1 to 20 μm (maximum 100 μm). In reflected light, the mineral color varies from whitish to pale yellow and pinkish gray. The reflectivity is lower relative to tennantite but higher relative to sphalerite and germanite. The mineral is isotropic. Cleavage and internal reflection are absent. The relative relief is close to that of germanite. The VHN_{30} value varies from 265 to 340 kg/mm^2 (average 295 kg/mm^2). Contents of Cu, Fe, Zn, and S are rather stable (Table 1). Element pairs Mo–W and Ge–As are characterized by negative correlations.

[1] Maikainite (IMA92.038) and ovamboite (IMA92.039) have been approved by the Commission on New Minerals of IMA on January 29, 1993. Notification of Ernst Burke (Chairman of CMN IMA) dated February 23, 2003.

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Table 1. Chemical compositions of maikainite (nos. 1–3) and ovamboite (nos. 4–7) from the Tsumeb deposit, Namibia (wt %)

Element	1	2	3	4	5	6	7
Cu	42.55	41.40	41.45	38.35	39.85	40.05	38.65
Ag	0.00	0.00	0.00	0.00	0.00	0.01	0.05
Fe	6.35	6.45	6.06	6.69	4.75	4.72	6.32
Zn	0.56	0.39	0.35	3.12	3.34	2.20	1.81
Mo	5.21	4.73	3.88	0.35	1.01	1.64	1.73
W	1.24	2.41	3.32	9.94	9.83	8.21	7.42
Sn	0.00	0.00	0.00	0.02	0.04	0.00	0.03
V	0.12	0.12	0.00	0.16	0.09	0.10	0.14
Ge	10.86	10.18	11.44	9.70	10.01	9.86	9.94
Ga	0.15	0.10	0.00	1.67	0.48	0.50	0.60
As	2.28	2.51	1.86	1.18	2.58	0.87	1.93
S	31.40	31.30	30.95	30.35	29.65	29.90	30.15
Total	100.72	99.59	99.31	101.53	101.63	99.42	98.77
Formula units based on 66 atoms							
Cu	21.91	21.62	21.83	20.41	21.41	21.67	20.87
Ag	–	–	–	–	–	–	0.01
Fe	3.72	3.83	3.63	4.05	2.91	2.91	3.89
Zn	0.28	0.20	0.18	1.61	1.74	1.16	0.95
Total	25.91	25.65	25.64	26.07	26.06	25.74	25.72
Mo	1.79	1.64	1.35	0.12	0.36	0.59	0.62
W	0.22	0.43	0.61	1.83	1.83	1.54	1.39
Sn	–	–	–	0.01	0.01	–	0.01
V	0.08	0.08	–	0.10	0.06	0.07	0.09
Total	2.09	2.15	1.96	2.06	2.26	2.20	2.11
Ge	4.90	4.65	5.27	4.52	4.70	4.67	4.70
Ga	0.07	0.05	–	0.81	0.24	0.92	0.30
As	0.99	1.11	0.83	0.53	1.17	0.40	0.88
Total	5.96	5.81	6.10	5.86	6.11	5.99	5.88
S	32.04	32.39	32.30	32.01	31.57	32.07	32.28

Note: Camebax microprobe (E.M. Spiridonov, analyst). Standards: Chalcostibite (Cu, S), bornite (Fe), synthetic ZnSe (Zn), WS_2 (W), MoS_2 (Mo), SnS_2 (Sn), Ge (Ge), GaAs (Ga, As), and hessite (Ag). Te, Se, Bi, and Sb were not detected.

However, (Mo + W) and (Ge + As) atomic contents are approximately constant. The ovamboite formula fits $Cu_{20}(FE,Zn,Cu)_6(W,Mo,V)_2(Ge,As,Ga)_6S_{32}$ in the general form and $Cu_{20}(Fe,Zn,Cu)_6W_2Ge_6S_{32}$ in the stoichiometric form. Its XRD pattern is close to that of germanite [13] and Ge-colusite [5]. Maximal reflections in the powder XRD image are as follows (Å): 3.08 (10) (222), 1.887 (7) (440), and 1.612 (5) (622) (Table 2). The cubic lattice has the following parameters: a_0 = 10.68 (2) Å, V = 1216 (4) Å^3, Z = 1, and X-ray density = 4.736 g/cm^3. Reflection spectra are characterized by complex patterns with a subhorizontal trend, which is responsible for the nearly neutral mineral color (Table 3).

In terms of chemical composition and XRD patterns, maikainite and ovamboite make up a continuous series. They are characterized by significantly lower Fe contents (relative to germanite), negligible V contents (relative to Ge-colusite), and significantly higher Mo and W contents (relative to germanite and Ge-colusite). Maikainite is distinguished from optically similar hemusite, stannite, and briartite by composition and reflection spectra. Ovamboite is similarly distinguished from kiddcreekite and colusite.

Table 2. XRD data on maikainite and ovamboite from the Tsumeb deposit (Fe/Mn; D = 114.7 mm)

hkl	Maikainite (analysis no. 1)			Ovamboite (analysis no. 5)		
	I	d_{meas}	d_{calc}	I	d_{meas}	d_{calc}
211	–	–		1	4.36	4.358
310	–	–		1	3.38	3.376
222	10	3.07	3.072	10	3.08	3.082
400	2	2.66	2.660	2	2.67	2.669
440	8	1.884	1.881	7	1.887	1.887
622	4	1.603	1.604	5	1.612	1.609
444	0.5	1.536	1.5359	1	1.543	1.5408
800	1	1.331	1.3301	1	1.333	1.3344
662	2	1.220	1.2206	1.5	1.225	1.2245
840	1	1.190	1.1897	0.5	1.192	1.1935
a_0, Å		10.64 ± 0.01			10.68 ± 0.02	
X-ray density, g/cm^3		4.543			4.736	

Note: Exposition sample was a "rubber globule" (diameter ~0.2 mm). Internal standard was NaCl.

Table 3. Spectra of maikainite and ovamboite reflectivity in air (R, %)

λ, nm	Maikainite	Ovamboite	
	analysis no. 1	analysis no. 4	analysis no. 5
400	22.3	22.1	23.0
420	22.7	22.4	23.3
440	23.4	22.8	23.7
460	23.4	23.2	24.1
470	23.7	23.1	24.0
480	24.1	23.1	23.9
500	24.8	23.2	24.1
520	24.9	23.5	24.2
540	25.4	23.6	24.3
546	25.5	23.7	24.3
560	25.6	23.8	24.4
580	25.7	24.0	24.5
589	25.7	24.0	24.4
600	25.6	24.0	24.3
620	25.1	24.3	24.1
640	25.4	23.9	24.3
650	25.6	23.8	24.0
660	25.7	23.8	23.7
680	25.0	23.7	23.9
700	23.8	23.9	24.2

Note: Blesk GOI microreflectometer (T.N. Chvileva, analyst). Standard was metallic silicon attested in GOI based on W–Ti carbide (the latter was attested in NPL, England).

Maikainite, ovamboite, germanite, and colusite have similar XRD patterns and compositions ($Me_{34}S_{32}$). The structure is correctly deciphered only for colusite with the following four positions [9]: $(Cu + Fe + Zn)_{26}$ (position 1), $(As + Sn + Ge\ldots)_6$ (position 2), $(S)_{32}$ (position 3), and (V_2) (position 4). The position of V in the colusite structure probably corresponds to that of Fe^{3+} in the germanite structure [3]. Maikainite and ovamboite have the following atomic sums: (Cu + Fe + Zn) = 26, (Ge + As + Ga) = 6, and (Mo + W) = 2. The positions of Mo and W in their structure are probably analogous to that of V in the colusite structure. Taking into consideration the requirement of electrical neutrality, probable formulas of maikainite and ovamboite are as follows:

maikainite $Cu_{20}^{1+}(Fe^{2+}, Cu^{2+})_6Mo_2^{4+}Ge_6^{4+}S_{32}$,

ovamboite $Cu_{20}^{1+}(Fe^{2+}, Zn, Cu^{2+})_6W_2^{4+}Ge_6^{4+}S_{32}$.

Thus, maikainite and ovamboite can be considered Mo- and W-analogues of germanite or Ge-colusite.

Samples of these minerals are deposited in the Mining Museum (St. Petersburg) and Fersman Mineralogical Museum (Moscow).

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