Malanite—A New Cupric Platinum (Pt^{3+}) and Iridium (Ir^{3+}) Sulphide

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Abstract Malanite was first found in veinlets of disseminated copper–nickel ores in Zunhua County, Hebei Province, and then in platinum–bearing chromite ores in Shuangfeng Village, Yanshan. In the former case, malanite appears as octahedrons or dodecahedrons associated with pyrrhotite, pentlandite, sperrylite and cooperite; while in the latter case, it is massive or present in anhedral glomerocrysts, filling in cracks of iridisite and associated with osmiride, ferrian platinum and iridisite. Malanite is steel–grey in colour, opaque with metallic lustre and black streaks and brittle with no magnetism. $H_M = 5.0$, $VHN_{20} = 417 kg/mm^2$, cleavage {111} sometimes observed. The calculated density is 7.57 g/cm^3. The reflective colour is white with a light green tint. Internal reflections are not observed. This mineral is isotropic, showing no bireflection or reflection pleochroism in air. By means of electron microprobe analysis, the empirical formula (based on 7 atoms) is expressed as $(Cu_{0.93}Fe_{0.06})_{\Sigma 0.99}(Pt_{1.03}Ir_{0.66}Rh_{0.04}Pd_{0.03}Co_{0.20}Ni_{0.03})_{1.99}S_{4.03}$ or $(Cu_{0.95}Fe_{0.07})_{\Sigma 1.02}(Pt_{1.37}Ir_{0.45}Co_{0.11}Rh_{0.08})_{\Sigma 2.01}S_{3.97}$. Five strongest lines (*hkl, d, I*) of X–ray powder diffraction data of malanite are 311,2.98 (6);400,2.48(5); 333,1.90(7); 440, 1.75 (10); 731, 1.29 (5). It was known on the basis of X–ray powder diffraction data that malanite is cubic, and the space group is Fd3m with $a = 0.9940$nm, $V = 0.9821$ (3) nm^3 and $Z = 4$. The type material of malanite is deposited at the Geological Museum of China (GMC)

Key words: new mineral, malanite, chrome ore

1 Occurrence

There are two modes of occurrence of malanite. (a) It occurs in disseminated nickel–copper sulphide ores in olivine pyroxenite dykes, associated with pyrrhotite, pentlandite, chalcopyrite, moncheite, sperrylite and cooperite, and (b) it is present in platinum–bearing chromite ores in dunite or as a constituent of placer concentrates near orebodies in Shuangfeng Village of Yanshan. Malanite is associated with osmium, native iridium, iridosmine, ferric platinum, cooperite and sperrylite.

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2 Appearance and Physical Properties

Malanite occurs as octahedral or dodecahedral euhedral crystals, 0.1–0.2 mm in diameter in nickel–copper sulphide ores. It is also found in chromite ores along cracks of iridisite (IrS_2) as veins replacing iridisite. Malanite exists as lumps ($200\times100\mu$, $100\times30\mu$, $80\times33\mu$) or veinlets with a width of $5-10\mu$ and a length of $100-200\mu$. Colour steel–grey; streak black; opaque; lustre metallic. Hardness $H_M=5.1$ and microhardness $VHN_{20}=417$ kg / mm^2 (ranging from 403–440 kg / mm^2); brittle. Cleavage {111} is observed sometimes with no fracture. Density cannot be measured directly due to small grain size. Density (calc.) = 7.57 g / cm^3.

Reflective colour of malanite is white with a greenish tint. No internal reflection is observed. It is isotropic. Bireflectance and reflection pleochroism are not shown in air. Reflectance was measured with a MPM 400 microphotometer made in Germany based on the WTiC standard issued by the Commission on Ore Microphotometer (COM). The obtained values are listed in Table 1 and the dispersive curve of reflectance is shown in Fig. 1.

Table 1 Reflectance values for malanite (sample 2)

λnm	R%	λnm	R%	λnm	R%
400	36.5	510	37.5	620	38.4
410	36.6	520	37.5	630	38.5
420	36.8	530	37.6	640	38.5
430	37.1	540	37.7	650	38.6
440	37.1	550	37.7	660	38.7
450	37.2	560	37.8	670	38.8
460	37.2	570	37.9	680	38.9
470	37.3	580	38.0	690	38.9
480	37.3	590	38.1	700	39.1
490	37.4	600	38.2		
500	37.4	610	38.3		

Note: S_E *Rvis* 37.9; *x* 0.336; *y* 0.335; *λd* 581.5; *Pe* 0.015; S_A *Rvis* 38.0; *x* 0.450; *y* 0.408; *λd* 591.8; *Pe* 0.020; S_C *Rvis* 37.8; *x* 0.312; *y* 0.317; *λd* 586.5; *Pe* 0.007.

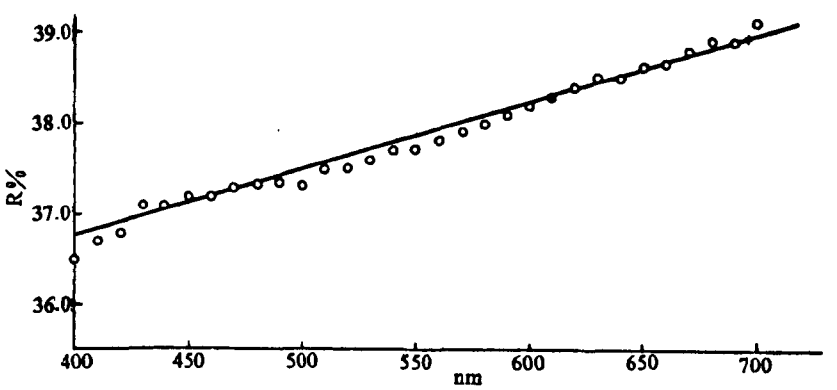

Fig. 1. Dispersive curve of the reflectance of malanite.

3 Chemical Composition

At first an Edax–9900 energy dispersive spectrometer was used for qualitative analysis and then JCMA–733 and EPMA–8705 electron microprobes were used for quantitative analysis with working voltage 20 kv. The analyses were performed at stable electric currents and beam currents, using pure metals Fe, Ni, Co, Cu, Rh, Pd, Os, Ir, Pt and S (pyrite) and Pb (galena) as the standards. The crystals used in the analysis were PET for S$K\alpha$, Rh$L\alpha$, Pd$L\beta$ and Pb$M\alpha$; LIF for Fe$K\alpha$, Co$K\alpha$, Os$K\alpha$, Ir$L\alpha$and Pt$L\alpha$; and TAP for As$L\alpha$. All the data were corrected by ZAF, which are listed in Table 2. The mean analytical results (and ranges) (%) for sample 2 are S 22.6 (21.9–23.3), Fe 0.7 (0.3–1.1), Co 1.1 (0.7–1.5), Cu 10.7 (9.9–11.7), Rh 1.5 (1.3–2.0), Ir 15.4 (14.0–17.3) and Pt 47.4 (45.8–48.9). The total is 99.4. The empirical formula (based on 7 atoms) is $(Cu_{0.95}Fe_{0.07})_{\Sigma 1.02}$ $(Pt_{1.37}Ir_{0.45}Co_{0.11}Rh_{0.08})_{\Sigma 2.01}S_{3.97}$. The mean analytical results (and ranges) (%) for sample 1 are S 23.8 (23.2–24.2), Fe 0.6 (0.2–0.9), Co 2.2 (1.7–2.7), Ni 0.3 (0.1–0.5), Cu 10.9 (10.1–11.8), Rh 0.7 (0.5–0.9), Pd 0.5 (0.3–0.9), Ir 23.2 (22.2–24.0) and Pt 37.0 (36.4–37.8). The total is 99.2. The empirical formula (based on 7 atoms) is: $(Cu_{0.93}Fe_{0.06})_{\Sigma 0.99}(Pt_{1.03}Ir_{0.66}Rh_{0.04}Pd_{0.03}Co_{0.20}Ni_{0.03})_{1.99}S_{4.03}$. The simplified formula is $CuPt_2S_4$, which requires S 22.0, Pt 67.1 and Cu 10.9. Total 100.00.

Table 2 Electron microprobe analyses data(%) for malanite

Sample	No.	S	Fe	Co	Ni	Cu	As	Ph	Pd	Os	Ir	Pt	Pb	Total
Sample 1	1	24.1	0.2	2.47	0.1	11.8	0.0	0.8	0.3	0.0	22.8	36.5	0.0	99.07
	2	24.2	0.3	2.11	0.2	11.1	0.0	0.7	0.3	0.0	23.9	36.4	0.0	99.21
	3	23.8	0.8	1.98	0.4	10.9	0.0	0.6	0.4	0.0	24.0	36.8	0.0	99.68
	4	23.9	0.9	1.73	0.5	10.8	0.0	0.5	0.5	0.0	23.1	37.5	0.0	99.43
	5	23.2	0.9	2.74	0.4	10.1	0.0	0.9	0.9	0.0	22.2	37.8	0.0	99.14
	Mean	23.8	0.6	2.21	0.3	10.9	0.0	0.7	0.5	0.0	23.2	37.0	0.0	99.21
Sample 2	1	22.4	0.8	0.7	–	10.2	–	1.5	0.0	–	15.1	48.9	–	99.6
	2	23.3	0.6	1.3	–	10.5	–	1.3	0.0	–	14.9	47.7	–	99.6
	3	23.1	0.3	1.1	–	11.1	–	2.0	0.0	–	14.3	47.9	–	99.8
	4	23.0	0.7	1.5	–	11.0	–	1.5	0.0	–	15.5	45.8	–	99.0
	5	22.0	0.5	0.9	–	10.9	–	1.7	0.0	–	15.7	47.4	–	99.1
	6	21.9	1.1	0.8	–	10.3	–	1.0	0.0	–	17.3	46.7	–	99.1
	Mean	22.6	0.7	1.1	–	10.7	–	1.5	0.0	–	15.5	47.4	–	99.5

Note: Sample 1 from nickel–copper sulphide ore and sample 2 from chromite ore.

4 X–ray Crystallography

X–ray powder diffractions were studied with Ni–filtered Cu radiation and Mn–filtered Fe radiation, yielding I and d values shown in Table 3. The analysis shows that malanite is a mineral of sulphospinel type. Powder diffraction data were indexed and malanite was determined to be cubic. The space group is $Fd3_m$ with a = 0.9940(3)nm, V = 0.9821 nm^3 (sample 2 in 1990), or a = 0.9910 nm, V = 0.9732(3)nm^3, and Z = 4 (sample 1 in 1974).

5 Conclusions

The new mineral malanite was discovered as early as 1972 and reported in *Acta Geological Sinica* in 1974 (Yu et al.). Because only a low-grade electron microprobe was used then, the analysis was actually qualitative. The chemical composition of malanite was determined as Pt-Ir disulphide and the unit cell and space group were wrongly calculated to be of pyrite type. This mistake was corrected in a paper published in *Dizhi Kuangchan Yanjin* (Yu, 1976). Dayingite ($CuPtCoS_4$), renamed cobalt-malanite afterwards (Yu, 1981), was also reported in the same paper. Both minerals belong to platinum sulphospinel type, but cobalt-malanite is different from malanite as the former contains cobalt equal to platinum in content. The indices of crystal face and size of unit cell were obtained by indexing the powder diffraction data of a sulphospinel mineral.

After malanite and dayingite were announced by the author, Peng Zhizhong et al. raised an objection in 1978, concerning the chemical composition, space group and unit cell of malanite (Peng et al., 1978). In fact that was not Peng' s original opinion. He had initially believed that trivalent Pt^3 of dayingite should not exist in nature. Since Peng' s paper came out after the author' s article the author thinks that he changed his original intention after he read the author' s paper. The indices of crystal face and size of unit cell he calculated are identical with the author' s corrected data.

Table 3 X-ray powder diffraction data for malanite

Sample 2, malanite a 0.9940 nm				Sample 1, malanite a 0.9910 nm			
I	$d_{meas.}$	$d_{cal.}$	*hkl*	I	$d_{meas.}$	$d_{cal.}$	*hkl*
4	5.72	5.739	111	5	5.70	5.72	111
1	3.50	3.514	220	1	3.50	3.50	220
6	2.98	2.997	311	6	2.98	2.99	311
5	2.48	2.485	400	8	2.48	2.48	400
7	1.90	1.913	333	8	1.90	1.91	333
10	1.75	1.757	440	10	1.75	1.752	440
3	1.69	1.680	531	1	1.67	1.675	531
2	1.51	1.516	533	2	1.50	1.511	533
2	1.43	1.435	444	1	1.43	1.430	444
1	1.38	1.392	551	1	1.38	1.388	551
1	1.31	1.328	642	1	1.31	1.324	642
5	1.29	1.294	731	2	1.288	1.290	731
2	1.240	1.243	800	3	1.240	1.239	800
1	1.203	1.205	644	1	1.200	1.202	644
2	1.146	1.1478	751	2	1.142	1.144	751
2	1.111	1.1113	840	2	1.110	1.108	840
1	1.091	1.0911	911	1	1.087	1.088	911
5	1.014	1.0145	844	7	1.011	1.011	844
1	0.999	0.9990	771	1	0.995	0.9960	771
	–		951	2	0.958	0.9580	951
	–		880	4	0.876	0.8759	880
	–		971	1	0.865	0.8658	971
	–		11.3.3	3	0.840	0.8406	11.3.3
	–		12.0.0	2	0.826	0.8258	12.0.0
	–		975	1	0.796	0.7960	975
	–		12.4.0	8	0.783	0.7835	12.4.0

Note: Sample 1 from nickel-copper sulphide ore and sample 2 from chromite ore.

Dayingite published in 1974 and corrected malanite in 1976 are Pt^{3+}– and Ir^{3+}–bearing sulphospinel minerals that were first reported in the world. At that time, even the artificial sulphospinel of platinum group elements (PGE) was only cupric rhodium sulphide, which came out in 1964.

Malanite was not approved when announced in 1974 and no definite information regarding its approval was learnt even when supplementary and corrected data were published in 1981 (Yu Zuxiang). In this research, financially supported by the National Natural Science Foundation of China, the author studied the malanite discovered at Shuangfeng Village in Yanshan and reported the result to the Commission on New Minerals and Minerals Names of the International Mineralogical Association (CNMMN), so that malanite was accepted by CNMMN in 1995 (No. 95–003).

Following discovery of dayingite (cobaltmalanite) and malanite, quite a number of new minerals of trivalent PGE have been found one after another in the world, such as bowieite discovered in Alaska, USA, in 1984 (Rudashevski, 1985) and cuprorhodsite (Rudashevski, 1985), cuproiridsite (Rudashevski, 1985), inaglyite and konderite in Russia in 1985. These minerals were also found in chrome–bearing ores in this region. They are associated with malanite, but inaglyite and konderite resulting from in–situ crystallization are often closely associated with bowieite. These minerals sometimes exhibit unmixing texture or replacement texture and enclose crystals of iridosmine. Later–crystallized cuprorhodsite and cuproiridsite occur as euhedral granular replacement iridisite, while malanite occurs as veinlets replacing or filling late iridisite.

The author believes that late–stage ore solutions of iridisite contain copper but are poor in lead, and malanite crystallized therefrom was precipitated along cracks in iridisite to form the latest platinum minerals. The author also considers that platinum ores in this region were deposited from alkali ore solutions under a more oxidized condition near surface. In this environment, platinum–group elements can easily change from bivalence into trivalence state so as to form a large number of minerals containing trivalent platinum–group elements in this region.

Simultaneously with the discovery of malanite, rhodomalanite ($CuRhPtS_4$) (a new variety of malanite) was found in this region, a detailed discussion of which will be given later.

Malanite is named after its locality, i.e. Malanyu Village in Zunhua County, Hebei province, and the type material is deposited at the Geological Museum of China (GMC).

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Explanation of Plate

Photographs 1–8 are all back-scattered electron image photos.

1. Massive malanite (black), injected along cracks in iridisite (greyish black), with polyxene groundmass (white). ×300.

2. Same as Photo 1. ×940.

3. Massive malanite (black), injected along cracks in iridisite (greyish black), with polyxene groundmass (white). ×320.

4. Same as Photo 2. ×540.

5–6. Subhedral-granular malanite in veinlets. ×400.

7–8. Subhedral-granular malanite in veinlets. ×780 and ×400.