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ZINCOSPIROFFITE, A NEW TELLURITE MINERAL SPECIES FROM THE ZHONGSHANGOU GOLD DEPOSIT, HEBEI PROVINCE, PEOPLE'S REPUBLIC OF CHINA

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ABSTRACT

Zincospiroffite ($Zn_2Te_3O_8$), a new tellurite mineral species, was discovered in the Zhongshangou gold deposit in Chongli County, Hebei Province, China. Since it has only been found as crystallite aggregates of hundreds to thousands of micrometers square in a single polished block, most work on the mineral had been carried out under the microscope. This mineral is intimately associated with calaverite and sphalerite, either as micrometric films coating calaverite or in irregular aggregates replacing calaverite. It is a product of secondary co-oxidation of calaverite, associated with sphalerite, pyrite, and other sulfides. It is a gray and translucent mineral, with a dark green streak and a vitreous luster, without internal reflections, and with a weak anisotropy, bireflectance and pleochroism. It is quite soft, has a brittle tenacity and an uneven fracture. Raman spectroscopy demonstrates that the mineral is a natural analogue of synthetic $Zn_2Te_3O_8$. An electron-microprobe analysis gave the following composition: ZnO 24.57, PbO 1.64, MgO 0.24, TeO_2 71.90, minor FeO and SeO_2, total 98.89 (in wt.%), corresponding to an empirical formula $(Zn_{1.97}Pb_{0.05}Mg_{0.04}Fe_{0.02})_{\Sigma 2.08}$ $(Te_{2.95}Se_{0.01})_{\Sigma 2.96}O_{8.00}$ or, ideally, $Zn_2Te_3O_8$. Powder X-ray diffraction gave only seven lines with weak intensities [*d* in Å(I)(*hkl*): 4.758(w)(110), 3.240(w)(31$\bar{1}$), 2.928(m)(113), 2.820(w)(20$\bar{4}$), 2.155(w)(023,511), 1.985(w)(223), 1.599(w)(42$\bar{5}$), which are similar to those of the synthetic $Zn_2Te_3O_8$ (PDF 44–0241). On the basis of the diffraction pattern, the following unit-cell parameters were obtained: *a* 12.72(4), *b* 5.15(1), *c* 11.82(3) (Å), β 99.2(3)°, *V* 764.57(2.52) Å^3, with $Z = 4$ and $D_{calc} = 5.57$ g cm^{-3}. With these parameters, a comparison is made of zincospiroffite, synthetic $Zn_2Te_3O_8$ and spiroffite. The new mineral and its name were approved by the Commission on New Mineral and Mineral Names of International Mineralogical Association (IMA 2002–047). The only polished section was housed under catalogue number M10442 in the collection of the Geological Museum of China.

Keywords: zincospiroffite, new mineral species, tellurite, Zhongshangou gold deposit, Dongping gold orefield, China.

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SOMMAIRE

Nous avons découvert la zincospiroffite ($Zn_2Te_3O_8$), nouvelle espèce minérale, dans le gisement aurifère de Zhongshangou, comté de Chongli, province de Hebei, en Chine. Ce tellurite se présente en aggrégats de cristallites sur une surface de centaines ou de milliers de micromètres carrés d'un seul bloc poli; la plupart de nos observations ont donc dû être faites sous le microscope. C'est un minéral intimement associé à la calavérite et à la sphalérite, soit sous forme de pellicules micrométriques recouvrant la calavérite, soit en aggrégats irréguliers remplaçant la calavérite. La zincospiroffite est attribuable à la co-oxydation secondaire de la calavérite, en association avec sphalérite, pyrite, et autres sulfures. Il s'agit d'un minéral gris et translucide, avec une rayure vert foncé et un éclat vitreux, sans réflexions internes, et avec une faible anisotropie, biréflectance et pléochroïsme. Sa dureté est relativement faible, mais elle possède une tenacité cassante et une fracture inégale. Les spectres de Raman démontrent qu'il s'agit de l'analogue naturel du composé synthétique $Zn_2Te_3O_8$. Une analyse obtenue avec une microsonde électronique a donné: ZnO 24.57, PbO 1.64, MgO 0.24, TeO_2 71.90, des quantités mineures de FeO et SeO_2, pour un total de 98.89% (poids), et une formule empirique de $(Zn_{1.97}Pb_{0.05}Mg_{0.04}Fe_{0.02})_{\Sigma 2.08}(Te_{2.95}Se_{0.01})_{\Sigma 2.96}O_{8.00}$ ou, de façon idéale, $Zn_2Te_3O_8$. Le spectre de diffraction X, méthode des poudres, a révélé que sept raies ayant de faibles intensités [*d* en Å(I)(*hkl*)I: 4.758(w)(110), 3.240(w)($31\bar{1}$), 2.928(m)(113), 2.820(w)($20\bar{4}$), 2.155(w)(023,511), 1.985(w)(223), 1.599(w)($42\bar{5}$); elles correspondent aux raies du composé synthétique $Zn_2Te_3O_8$ (PDF 44–0241). Ces raies mènent aux paramètres réticulaires suivants: *a* 12.72(4), *b* 5.15(1), *c* 11.82(3) (Å), β 99.2(3)°, *V* 764.57(2.52) $Å^3$, avec $Z = 4$ et $D_{calc} = 5.57$ g cm^{-3}. Avec ces paramètres, nous sommes en mesure de comparer la zincospiroffite, le $Zn_2Te_3O_8$ synthétique et la spiroffite. Le nouveau minéral et le nom ont reçu l'approbation de la Commission des Nouveaux Minéraux et des Noms de Minéraux (IMA 2002–047). L'unique lame mince est conservée dans la collection du Musée géologique de Chine, numéro M10442 dans son catalogue.

(Traduit par la Rédaction)

Mots-clés: zincospiroffite, nouvelle espèce minérale, tellurite, gisement aurifère de Zhongshangou, champ minéralisé de Dongping, Chine.

INTRODUCTION

We report the discovery of zincospiroffite, $Zn_2Te_3O_8$, the zinc-dominant analogue of spiroffite (Mandarino *et al.* 1963) in a polished section of ore from the Zhongshangou gold deposit, Chongli County, Hebei Province, People's Republic of China. We used the electron microprobe and the Raman spectrophotometer for the *in situ* analysis and characterization of zincospiroffite before the mineral was dug out for powder X-ray diffraction. The physical, chemical, and powder-diffraction data establish zincospiroffite as a new mineral species. The new mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA 2002–047). The name *zincospiroffite* reflects its similarity in unit-cell parameters and bulk composition to spiroffite, a mineral discovered in Mexico in which variable amounts of zinc substitute for manganese, which is the dominant divalent cation (Mandarino *et al.* 1963, Cooper & Hawthorne 1996). The only thin section is housed in the collection of the Geological Museum of China in Beijing under catalogue number M10442.

OCCURRENCE

The Zhongshangou gold deposit, located at 115°05'E longitude and 40°55'N latitude, is one of the tellurium-bearing gold deposits in the Dongping gold orefield, an important gold producer in China (Nie 1998, Miller *et al.* 1998). Many tellurium oxysalts have been sampled and investigated for their mineral processing behavior (Cai 1996, Zhang *et al.* 2002a,b). These oxysalts occur as secondary products of the co-oxidation of calaverite and sulfides in quartz-vein-type gold ores.

Zincospiroffite was accidentally discovered in one polished section of ore. It occurs in three aggregates of crystallites covering an area of 400–4000 μm^2. These aggregates contain micrometric grains of native gold, also produced during the oxidation of an assemblage calaverite + sphalerite ± pyrite in quartz (Fig. 1). One of the aggregates is coated by hematite.

PHYSICAL AND OPTICAL PROPERTIES

As the crystallites of zincospiroffite occur in micrometric aggregates, it is difficult to determine the appearance and physical properties of this mineral. The following are some aspects obtained from two of the three aggregates in the polished sample before they were dug out for powder X-ray diffraction. The mineral is gray and translucent, with a dark green streak and vitreous luster. It shows weak anisotropy, bireflectance and pleochroism, and no internal reflections. It is quite soft, brittle with an uneven fracture. For the largest aggregate (15×350 μm^2), ranges of reflectance values were determined in the air, with a crystal of SiC_4 as a standard (Table 1).

CHEMICAL COMPOSITION

Back-scattered electron images (Fig. 1) were obtained using a S–3500 scanning electron microscope equipped with a LINK300 energy-dispersion spectrometer at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The images show the crystallites of zincospiroffite to be chemically homogeneous. For two aggregates of zincospiroffite, analyses were made *in situ* using a JXA–8800M electron microprobe equipped with wavelength-dispersion spectrometers at the State Key Laboratory for Mineral Deposits Research, Nanjing University. The analytical conditions were: acceleration voltage 15 keV, beam spot 1 μm^2, current 2.0×10^{-8} A, and counting time 15 seconds, with calibration as shown in Table 2. The amounts of H_2O and CO_2 were not measured by the wet-chemical technique, and their presence was ruled out by infrared and Raman spectroscopy under the microscope. The analytical data show consistent chemical compositions for two aggregates, except for Au and Fe contents in one aggregate (Fig. 1a), which are possibly caused by a hematite film and gold grains on its surface. Table 2 gives compositions expressed in weight percentages, and empirical formulae on the basis of 8 atoms of oxygen per formula unit.

RAMAN SPECTRA

Raman spectra have proved to be effective in the characterization of the short-range structure of materials and meteorite minerals (Sekiya *et al.* 1994, Chen *et al.* 1996). Raman spectra of the micrometric aggregates of zincospiroffite were compared with those of synthetic $Zn_2Te_3O_8$ and $ZnO–TeO_2$ glass before one aggregate was dug out for powder X-ray diffraction. All three aggregates were analyzed *in situ* with a Renishaw MK1–1000 laser Raman spectrophotometer at the China University of Geosciences in Wuhan. The sample was excited with an Ar^+ laser at 514.5 nm, with input power of 20 mW and a beam of 1 μm^2 filtered through a slit width of 12.5 μm. Figure 2 shows the Raman spectra for wavenumbers ranging from 100 to 1500 cm^{-1}. The wavenumbers beyond 1500 cm^{-1} were omitted, as no

TABLE 1. RANGES OF MEASURED VALUES OF REFLECTANCE FOR ZINCOSPIROFFITE*

λ nm	Rmin	Rmax	λ nm	Rmin	Rmax
400	22.3	29.7	560	6.9	6.9
420	12.7	16.1	580	6.4	6.4
440	6.9	8.6	589 (COM)	6.1	6.2
460	6.7	7.3	600	5.9	6.0
470 (COM)	7.0	7.5	620	5.4	5.6
480	7.4	7.7	640	4.8	5.3
500	7.6	7.9	650 (COM)	4.4	5.0
520	7.6	8.1	660	4.1	4.6
540	7.4	7.8	680	3.6	4.2
546 (COM)	7.1	7.3	700	3.1	3.7

Measured in air with SiC_4 crystal as a standard at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The standard wavelenths (COM) are indicated. Reflectance is quoted in %.

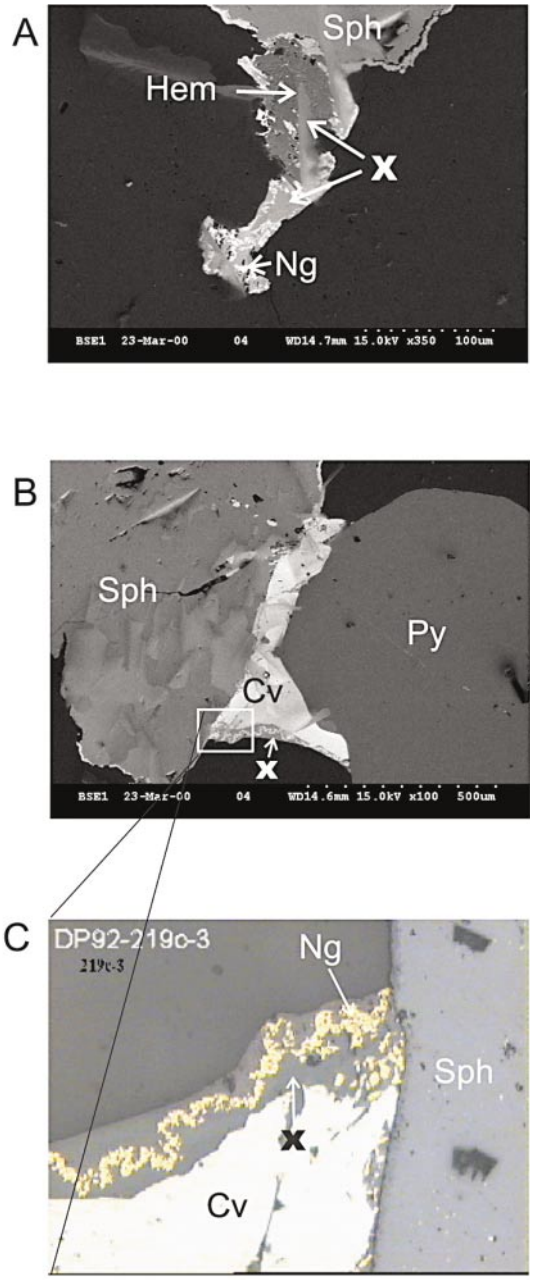

FIG. 1. BSE images (A,B) and color picture (C) showing zincospiroffite intergrown with native gold as the oxidation products of calaverite + sphalerite ± pyrite in the quartz ore of the Zhongshangou gold deposit, Chongli County, Hebei Province, China.

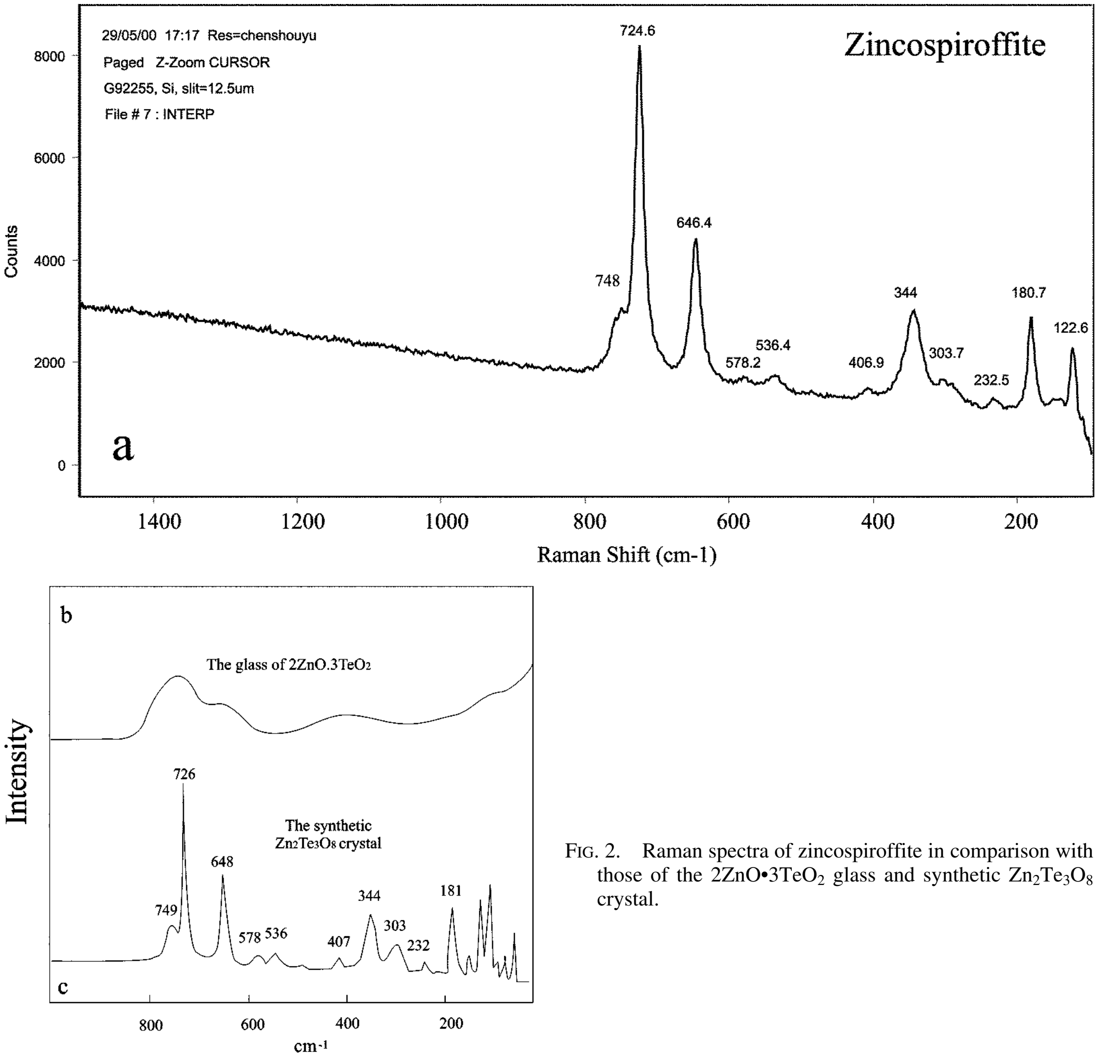

FIG. 2. Raman spectra of zincospiroffite in comparison with those of the $2ZnO•3TeO_2$ glass and synthetic $Zn_2Te_3O_8$ crystal.

peaks of H_2O were recorded. Figure 2 clearly demonstrates the consistency of scans of zincospiroffite with those of synthetic $Zn_2Te_3O_8$, and the lack of agreement with the $2ZnO•3TeO_2$ glass in terms of peak positions, intensities and half-widths of Raman spectra. Based on the Raman spectra, tellurium was calculated as TeO_2 in the electron-microprobe data.

X-RAY-DIFFRACTION SPECTRA

The largest aggregate was dug out with a needle under the microscope and mounted on a Debye–Scherrer camera 114.6 mm in diameter for powder X-ray diffraction with Cu$K\alpha$ radiation at the Geological Survey of Canada by Mr. Andrew C. Roberts. Although diffraction lines are weak relative to those of secondary gold trapped in zincospiroffite, seven lines were recognized; these lines match those of synthetic $Zn_2Te_3O_8$ (PDF44–241) and compare with those of spiroffite (Table 3). In principle, these seven lines are not sufficient for a meaningful unit-cell refinement. Nevertheless, we tentatively calculated the unit-cell parameters and density using the UnitCell refinement program by Holland & Redfern (1997); the results are listed in Table 3.

DISCUSSION AND CONCLUSION

The unit-cell parameters of synthetic $Zn_2Te_3O_8$, determined by Hanke (1966), are compared with those of spiroffite ($[Mn,Zn]_2Te_3O_8$). It is monoclinic, with a space group of *C2/c*. Its *a*:*b*:*c* ratio is 2.47: 1: 2.29, with b = 5.15 Å and β = 99.3°, and its unit-cell volume and density are calculated as 764.57 Å^3, and 5.57 (g/cm^3) with Z = 4.

TABLE 2. CHEMICAL COMPOSITION OF ZINCOSPIROFFITE

Constituent	Range $n = 6$	Mean	Standard deviation	Probe standard
TeO_2 wt.%	70.74 – 73.03	71.90	0.73	TeO_2
SeO_2	0.10 – 0.22	0.17	0.05	ZnSe
SO_2	0.00 – 0.07	0.03	0.03	$SrSO_4$
ZnO	23.67 – 26.60	24.57	1.04	ZnO
PbO	1.28 – 2.22	1.64	0.35	$PbCO_3$
MgO	0.15 – 0.32	0.24	0.06	MgO
FeO	0.00 – 0.84	0.20	0.33	Fe_2O_3
CaO	0.00 – 0.05	0.02	0.02	$CaSiO_3$
MnO	0.00 – 0.04	0.01	0.02	MnO
Au_2O	0.00 – 0.67	0.11	0.27	Pure gold
Total		98.89		

Empirical formula based on O = 8: $(Zn_{1.97}Pb_{0.05}Mg_{0.04}Fe_{0.02})_{2.08}(Te_{2.95}Se_{0.01})_{2.96}O_{8.00}$. The analyses were made with a JXA-8800M electron microprobe with wavelength-dispersion spectrometry at the State Key Laboratory for Mineral Deposits Research at Nanjing University.

TABLE 3. PROPERTIES OF ZINCOSPIROFFITE IN COMPARISON WITH THOSE OF SPIROFFITE AND SOME SYNTHETIC MATERIALS

	Zincospiroffite $Zn_2Te_3O_8$	Synthetic $Zn_2Te_3O_8$	Spiroffite $(Mn,Zn)_2Te_3O_8$	Synthetic $Mg_2Te_3O_8$
a (Å)	12.72(4)	12.676(1)	12.870(2)	12.493(2)
b (Å)	5.15(1)	5.198(1)	5.3813(5)	5.182(6)
c (Å)	11.82(3)	11.781(1)	11.888(2)	11.581(1)
β (°)	99.2(3)	99.6(1)	98.22(1)	98.6(1)
V Å^3	764.57(2.52)	765.38	814.8(2)	741.3(1.3)
S.G.		$C2/c$	$C2/c$	
Z	4	4	4	4
D (g cm^{-3})	5.57 (calc.)	5.568 (calc.)	5.059 (calc.)	
	d in Å (intensity) [*hkl*]			
	4.758(w)[110]	4.9734(31)[110]		4.77(70)[110]
	3.240(w)[31$\bar{1}$]	3.9372(23)[202]	4.98(S+)[110]	4.49(51)[11$\bar{1}$]
	2.928(m)[113]	3.2403(26)[31$\bar{1}$]	3.00(S+)[004]	3.905(68)[202]
	2.820(w)[20$\bar{4}$]	2.9234(100)[113]	4.06(S)[202]	3.206(76)[31$\bar{1}$]
	2.155(w)[023,511]	2.8191(22)[20$\bar{4}$]	3.31(S)[$\bar{3}$11]	2.901(84)[113]
	1.985(w)[223]	[511,020,023]*	1.63(M)	2.761(32)[20$\bar{4}$]
	1.599(w)[42$\bar{5}$]	1.6006(25)[42$\bar{5}$]		2.144(25)[511]

Zincospiroffite: found in the Zhongshangou gold deposit, Chongli, Hebei, China. The powder-diffraction lines were obtained with a Debye–Scherrer camera 114.6 mm in diameter (Cu$K\alpha$ radiation). Unit-cell parameters were refined with the program UnitCell (Holland & Redfern 1997).

Synthetic $Zn_2Te_3O_8$: Synthesized in hydrothermal system at a pH of 8 at 230°C. The unit-cell parameters are taken from PDF44–241. *: the intensity of these reflections is between 16 and 18.

Spiroffite: found in Moctezuma, Sonora, Mexico and named by Mandarino *et al.* (1963). The unit-cell parameters pertain to a single crystal whose structure was refined by Cooper & Hawthorne (1996).

Synthetic $Mg_2Te_3O_8$: Synthesized "dry" in the system MgO–TeO_2 at 680–750°C, and detected by Tromel & Ziethen-Reichnach (1970). The unit-cell parameters were refined with the program UnitCell (Holland & Redfern 1997).

Unlike spiroffite, $Mn_2Te_3O_8$, with its variable contents of zinc (Mandarino *et al.* 1963, Cooper & Hawthorne 1996), zincospiroffite does not contain any detectable manganese. Considering the similarity in crystal structure between $Mg_2Te_3O_8$ and $Zn_2Te_3O_8$, and the isomorphic substitution of zinc for manganese in spiroffite, zincospiroffite may be considered as the zinc-dominant analogue of spiroffite; a magnesium analogue ($Mg_2Te_3O_8$) of spiroffite awaits discovery.

In the only polished section, zincospiroffite occurs either as a rim on, or a replacement of, calaverite, associated with specks of gold in the rim or replacement. We believe that zincospiroffite and its specks of gold are products of oxidation of calaverite in association with sphalerite, pyrite, and galena. Research on the formation and dissolution of zincospiroffite may provide a clue to more efficient leaching of gold from the gold telluride ore in the Dongping gold orefield and "refractory gold" ores worldwide (Spry & Thieben 2000, Zhang *et al.* 2002a, b).

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