The mineralogical characterization of argentian cryptomelane from Xiangguang Mn-Ag deposit, North China

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Argentian cryptomelane as a quite rare variety is determined during the investigation of Mn-Ag ore samples from Xiangguang deposit along the northern margin of North China craton. The mineral observed by a polarizing petrographic microscope involves concentric ring-band, pisolitic and veinlet structures and greyish white color. The scanning electron microscopy reveals a large number of elongated nanocrystals in the forms of nanofibers and nanorods in this densely natural argentian cryptomelane. The specifically chemical features in two samples of XG-C-1 and XG-C-2 of cryptomelane are:

(1) $(K_{0.55}Na_{0.08}Ca_{0.06}Zn_{0.04}Ag_{0.03}Pb_{0.02}Mg_{0.01})_{0.79}(Mn_{7.21}Fe_{0.52}Al_{0.09}Si_{0.09})_{7.91}O_{16} \cdot nH_2O$;

(2) $(K_{0.37}Ca_{0.28}Ag_{0.13}Na_{0.07}Mg_{0.07}Zn_{0.06}Cu_{0.02})_{1.00}(Mn_{7.01}Fe_{0.40}Al_{0.39}Si_{0.03}Ti_{0.01}Cr_{0.01})_{7.85}O_{16} \cdot nH_2O$.

The silver content ranges from about 0.22–3.15 wt%, which is much higher than that of other manganese oxides including ranciéite, chalcophanite and coronodite found in this deposit as well. Both of two argentian cryptomelane samples feature two main Raman scattering contributions at about 580 cm^{-1} and 630 cm^{-1} , belonging to the Mn–O lattice vibrations within the MnO_6 octahedral double chains, which can distinguish from other three manganese oxides. The Ag^+ prefers to locate in the tunnel sites substituting K^+ of cryptomelane due to its large radius and the same monovalent state with K^+ . Some chain-width disorders characterized by transmission electron microscopy are probably caused by these cation substitutions.

Keywords: Cryptomelane, Silver, Mineralogical characterization, Xiangguang deposit, Raman spectroscopy

INTRODUCTION

Manganese oxide minerals are ubiquitous in a wide variety of geological setting, but silver-bearing manganese oxides are considered as quite rare mineral phases. Radtke et al (1967) first described ‘Aurorite’ $[(Mn,Ag,Ca)Mn_3O_7 \cdot 3H_2O]$ with chalcophanite structure as a new mineral at the Aurora mine, the Ag content of which can reach 7.5 wt% (Ag_2O). An argentian todorokite (3.9 wt% Ag_2O) and unnamed silver bearing lead manganese oxide (1.2 wt% Ag_2O) were also reported in these black calcite veins. At the San Miguel Tenango mine Ag was described by Gómez-Caballero et al (2010) to occur as nanometric particles of native silver adsorbed on the external surfaces of todorokite and of the amorphous phase.

All these kinds of silver-bearing manganese oxides

are mainly found in Mn-Ag type deposits. So far over fifteen kinds of manganese oxides have been identified in the worldwide Mn-Ag deposits, but the content results indicate only a few kinds such as cryptomelane, coronadite, todorokite and chalcophanite carry most of the silver (Radtke et al., 1967; Hildebrand and Mosier, 1974; Li et al., 1996). The complex occurrences and distributions of Ag associated with fine-grained Mn oxide minerals also contribute to the problems of low recovery in the metallurgical process despite high Ag grades (Gómez-Caballero et al., 2010; Tian et al., 2012).

Cryptomelane ($K_xMn_{8-x}O_{16}$, where $0.2 \leq x \leq 1$), essentially potassium manganese oxide, is the most abundant mineral of supergene manganiferous ore (Post, 1999). Argentian cryptomelane as a new variety was only reported to be found containing a few ppm to 1 wt% Ag in the Silver Cliff mining district of Colorado (Anderson et al., 1973). A silver content of 1 wt% produces no observable structural change at this mine (Hildebrand and

Mosier, 1974). The natural samples from Colorado exhibit very similar coordination distances as the synthetic cryptomelane which silver ions were sorbed onto (Ravikumar et al., 1998). Recently manganese oxides with the cryptomelane structure modified with silver have been demonstrated as Ag-hollandite ($\text{Ag}_x\text{Mn}_8\text{O}_{16}$, where $1 \leq x \leq 1.8$) by many material scientists. The Ag^+ center in a tunnel consisting of double chains of edge-sharing MnO_6 octahedra has the potential to be electrochemically and catalytically active (Takeuchi et al., 2012, 2013; Özacar et al., 2013). The presence of silver causes partial replacement of potassium from the channels and distortion of the cryptomelane structure (Gac, 2006). The cube-like cavities are created by face-sharing cubes of O^{2-} atoms with Ag atoms occupying the shared faces of the O^{2-} cubes. The occupancy of the Ag atoms at the shared faces of the cube-like cavities yields a peculiar square planar Ag^+ environment with bond distances of approximately 2.7 Å, which are a little larger than $\text{Ag}^+-\text{O}^{2-}$ (2.35 Å) (Takeuchi et al., 2012).

In this communication we characterize argentinean cryptomelane in Mn-Ag ores from the Xiangguang deposit, North China. The silver content is evaluated from 0.22–3.15 wt% in cryptomelane which is much higher than that in other manganese minerals of ranciéite, chalcophanite and coronadite found in the deposit. The aim of the present work is to provide a framework for better understanding distribution of Ag and possible substitution mechanisms for Ag incorporation. It may give more information on the metallurgical process and the origin of mineralization.

OCCURENCE

Specimens were collected from Xiangguang deposit, Hebei Province, which is typically related to volcanic and subvolcanic epithermal deposits along the northern margin of North China craton (Fig. 1). The area is located in the southwest of Xiaofanshan syncline in Yanshan fold belt and southeast of Xiangguang Mesozoic volcanic rift basin. Mn-Ag mineralization is strictly controlled by NNW-striking and NE-dipping compression-shear structural zone. The orebodies occur and develop largely at the site of the structural fracture zone especially at the cross section of unconformity between Zhangjiakou and Houcheng Formations. The igneous rocks in this area include extrusive rocks of rhyolitic ignimbrite and intrusive rocks of granite porphyry. Quartzitification – clayization – limonitization and propylitization are the two main types of the wall rock alteration, and the former type is highly close to Mn-Ag mineralization. The Mn-Ag orebodies are mainly hosted within tuffaceous greywacke in Zhangjiakou For-

mation and rhyolitic ignimbrite and granite porphyry in Houcheng Formation of Jurassic (Liu et al., 2012). The collected ores are classified into two types: a Mn-Ag ore and an alteration ore, in both of which the mineral assemblages are essentially the same but the relative contents have some variation.

EXPERIMENTAL

The epoxy-impregnated thin-sections of ore specimens were examined with both reflected and transmitted light with a Leica optimal microscope. The magnified details of selected zones were subsequently observed with Quanta 650 FEG and FEI Nano scanning electron microscope (SEM) with energy-dispersive spectrometry (EDS) and back-scattered electron (BSE) imaging capabilities. The quantitative mineral chemistry was analyzed using a JXA-8230 Electron probe by wavelength-dispersive spectrometry (EMPA). Operating conditions were an accelerating voltage of 15 kV, a beam current of 20 nA and a beam diameter about 2–5 µm. The analysis of Ag content was carried out on the Finnigan Element II double focusing magnetic sectorfield ICP-MS equipped with a high-performance New Wave 193 nm ArF excimer laser-ablation system in spot ablation with size of 40 µm (LA-ICP-MS). Calibration was performed using the silicate glass standards of NIST610 and KL2G. The raw analytical data were corrected for instrument drift and converted to concentration values using known values of manganese as an internal standard by the formula:

$$C_u^{sam} = \frac{k_u C_i^{sam} I_u^{sam}}{I_i^{sam}}.$$

In this formula k = relative sensitivity factor of element analyzed; C = concentration; sam = unknown sample; I = counts per second; u = element analyzed; i = internal standard element. The mineral identification was carried out with powder X-ray diffraction (XRD) using a RIGAKU-RA diffractometer with Cu X-ray source. The Raman spectrums of manganese oxides between 100 cm^{-1} and 3600 cm^{-1} were recorded using a Horiba Jobin-Yvon LabRAM HR800 system with a wavelength of 632 nm and spot sizes of 2–3 µm. A JEOL JEM-2010 microscope was used for high resolution transmission microscopy (HRTEM) and operated at 120 keV to examine cryptomelane crystal structure. Small amounts of manganese oxides for analysis were removed from specimens by micro-drilling tools. A drop of the resulting suspension in ethanol was placed on a holey carbon film supported by a TEM Cu grid.

Figure 1. Simplified geological map of Xiangguang Mn-Ag deposit (referenced from Liu et al., 2012). 1, sediment (Quaternary); 2, sandstone, conglomerate, dolomitic breccia in Houcheng Formation and rhyolitic ignimbrite, siltstone, conglomerate in Zhangjiakou Formation (Jurassic); 3, limestones intercalated with shales (Cambrian); 4, dolomite intercalated with shales and banded chert (Proterozoic); 5, granite porphyry, quartz porphyry, syenite porphyry breccia and diorite (Jurassic); 6, tectonic boundary of paleo volcanos; 7, fault; 8, the boundary of the deposit.

RESULTS

Appearance

The physical characteristics of silver-bearing cryptomelane are recognized as dull black on the surface, steel-gray to bluish-gray color on fresh fracture, brownish-black for streak, hardness of 6–7. Under a microscope it occurs as veins (Fig. 2a), nodules (Fig. 2b), colloform banding and concentric rings (Fig. 2c) with greyish white to light brown reflected color. SEM images show the grain dimensions and features of cryptomelane go into the nano-range. The crystals extend along one direction with various morphologies of rice-shaped rods (Fig. 2d) to wavy, fibrous forms (Fig. 2e) in the sample entitled XG-C-1, or align into two-dimensional plate or sheet configuration in the sample entitled XG-C-2 (Fig. 2f).

Chemical compositions

Two groups of EMPA data in Table 1 exhibit the difference of cryptomelane compositions. The contents of K_2O in XG-C-1 are 3.23–4.03 wt% which are close to reported 3.05–3.35 wt% in the natural cryptomelane from Xiangtan manganese deposit in China (Lu et al., 2003). However, the K_2O contents are lower (1.90–2.90 wt%) but CaO contents (1.01–2.44 wt%) are higher in XG-C-2 than those in XG-C-1. Since the EMPA cannot distinguish Mn^{2+} , Mn^{3+} from Mn^{4+} , we contribute total Mn to MnO_2 form due to only minor Mn^{2+} , Mn^{3+} in cryptomelane. The general empirical formula for the argentine cryptomelane calculated on the basis of $O = 16$ can be written as

Figure 2. Reflected-light (a), (b), (c) and SEM (d), (e), (f) photomicrographs of argentian cryptomelane from Xiangguang deposit. (a) veinlet structure; (b) nodular structure; (c) colloform banding; (d) rice-shaped rod habit; (e) fibrous habit; (f) nanorod and plate habit.

Table 1. Electron microprobe analyzer (EMPA) data (wt%) of cryptomelane

XG-C-1	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	PbO	Fe ₂ O ₃	TiO ₂	ZnO	BaO	Ag ₂ O	CuO	NiO	MnO ₂	Cr ₂ O ₃	Total
1	0.46	0.02	0.35	0.73	3.40	0.33	0.62	4.62	0.03	0.39	0.00	0.39	0.00	0.01	87.09	0.05	98.49
2	0.34	0.06	0.43	0.26	3.51	0.36	0.49	5.22	0.00	0.35	0.10	0.43	0.00	0.00	87.34	0.04	98.92
3	0.29	0.04	0.69	0.36	3.39	0.52	0.84	6.54	0.00	0.36	0.36	0.50	0.00	0.00	83.77	0.01	97.65
4	0.20	0.08	1.23	1.92	3.23	0.59	1.13	7.97	0.05	0.46	0.16	0.34	0.00	0.00	78.99	0.14	96.48
5	0.34	0.04	0.43	0.40	3.56	0.45	0.37	6.37	0.07	0.34	0.00	0.44	0.08	0.00	85.48	0.00	98.38
6	0.67	0.07	0.28	0.14	4.03	0.20	0.10	2.28	0.00	0.56	0.00	0.34	0.00	0.00	92.39	0.00	101.07
7	0.21	0.09	1.37	2.11	3.74	0.46	0.17	5.53	0.00	0.31	0.03	0.48	0.01	0.01	85.93	0.04	100.49
8	0.27	0.05	0.47	0.23	3.47	0.56	0.43	6.72	0.00	0.59	0.13	0.43	0.00	0.12	85.19	0.12	98.79
Average	0.35	0.06	0.65	0.77	3.54	0.44	0.52	5.66	0.02	0.42	0.10	0.42	0.01	0.02	85.77	0.05	98.78
XG-C-2	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	PbO	Fe ₂ O ₃	TiO ₂	ZnO	BaO	Ag ₂ O	CuO	NiO	MnO ₂	Cr ₂ O ₃	Total
1	0.35	0.43	2.64	0.25	2.42	2.26	0.00	4.32	0.19	0.58	0.07	1.87	0.26	0.06	80.70	0.18	96.56
2	0.33	0.43	2.63	0.26	1.90	2.44	0.00	5.56	0.00	0.73	0.00	1.59	0.18	0.00	77.90	0.22	94.16
3	0.38	0.38	2.32	0.16	2.04	2.13	0.15	3.79	0.00	0.47	0.00	1.68	0.13	0.02	78.51	0.00	92.15
4	0.20	0.41	2.43	0.15	2.32	2.16	0.03	3.37	0.00	0.49	0.00	1.75	0.21	0.02	76.85	0.05	90.44
5	0.24	0.35	2.93	0.19	2.10	1.95	0.00	5.63	0.00	0.46	0.03	1.73	0.26	0.00	75.64	0.06	91.57
6	0.15	0.22	2.47	0.18	2.90	1.01	0.06	2.44	0.15	0.35	0.03	3.01	0.26	0.00	85.09	0.09	98.43
Average	0.28	0.37	2.57	0.20	2.28	1.99	0.04	4.19	0.06	0.51	0.02	1.94	0.22	0.02	79.12	0.10	93.89

The Ag contents in cryptomelane have been compared by LA-ICP-MS with ranciéite, chalcophanite and coronadite which also occur in this deposit (Table 2). The results show silver is remarkably concentrated in cryptomelane. Its concentrations are from ten to hundreds of

times higher than those of other manganese oxides. The maximum amount of silver in cryptomelane as shown in Table 2 is 3.14 wt%. From the EDS maps in Figure 3 the occurrence of Ag correlates positively to Mn and shows a uniform distribution in cryptomelane. Small amounts of other cations as Pb, Zn, Ca and Fe are also present in it.

Table 2. Ag summary statistics of LA-ICP-MS analyses of different manganese oxide minerals from Xiangguang deposit

Mineral (sample No.)	Datapoints	Ag ($\mu\text{g/g}$)
Ranciéite	14	Max 82.3
		Min 46.5
		$[X] \pm \sigma$ 60.3 ± 14.2
Chalcophanite	17	Max 538.8
		Min 83.9
		$[X] \pm \sigma$ 250.0 ± 150.7
Coronadite	19	Max 319.6
		Min 133.3
		$[X] \pm \sigma$ 209.4 ± 44.6
Cryptomelane (XG-C-1)	12	Max 5442.5
		Min 2195.9
		$[X] \pm \sigma$ 3817.0 ± 969.8
Cryptomelane (XG-C-2)	14	Max 31469.4
		Min 12050.4
		$[X] \pm \sigma$ 18103.3 ± 6089.3

X-ray powder diffraction data

Although the powder sample was selected as homogeneous as possible using micro-drilling tools and presents a typical grey-black color of manganese oxide mineral, XRD patterns still often obtain lines of admixture components. X-ray diffraction analysis with a detection limit of about 5% indicates the presence of cryptomelane, quartz, and microcline in the sample XG-C-1 (Fig. 4). The diagnostic reflexes with d -values ($\text{\AA}$) of 6.95, 4.97, 3.12 and 2.40 for cryptomelane in XG-C-1 are recognized in Figure 4 and other characteristic reflexes are also exhibited in Table 3. It is very difficult for routine XRD analysis to identify argentine cryptomelane in XG-C-2 due to its poor crystallinity and strong interference from silicate minerals. So a series of Raman experiments are executed to examine the manganese mineral phases using thin-sections of ore specimens.

Raman spectroscopy

No obvious Raman band at the $1000\text{--}3600\text{ cm}^{-1}$ spectral region is observed. So the Raman spectrums of argentine cryptomelane between 100 cm^{-1} and 800 cm^{-1} are recorded and compared with ranciéite, chalcophanite and coronadite in Figure 5. Argentine cryptomelane have several contributions at 577 (583), 628 (630), 509, 380 (386), 273 (279) and $183\text{ (184)}\text{ cm}^{-1}$ in our samples. They give similar Raman responses with published data of cryptomelane shown in Table 4. All these six Raman

Figure 3. EDS maps of argentine cryptomelane in the sample XG-C-2.

bands can be attributed to the Mn-O lattice vibrations within the MnO_6 octahedral double chains. $\alpha\text{-MnO}_2$ type materials which cryptomelane belongs to have two diagnostic Raman active bands at high-frequency region, 574 cm^{-1} and 634 cm^{-1} . They are due to the symmetric Mn-O vibrations and are assigned to the A_g spectroscopic species (Julien et al., 2003; Gao et al., 2008, 2009). The Raman band at $634\text{ (628, 630 in this paper)}\text{ cm}^{-1}$ might

Figure 4. Powder X-ray diffraction of argentinean cryptomelane in the sample XG-C-1. Arrows denote the diagnostic diffraction peaks of cryptomelane.

Table 3. X-ray powder diffraction data for argentinean cryptomelane from Xiangguang Mn-Ag deposit

Cryptomelane(XG-C-1)		PDF Card No. 44-1386		
d (Å)	Relative intensity	d(Å)	hkl	Relative intensity
6.948	63	6.892	(101)	10
4.965	47	4.977	(200)	14
3.121	65	3.122	(301)	39
2.419	68	2.410	(21 $\bar{1}$)	40
2.402	100	2.400	(211), (11 $\bar{2}$)	100
2.392	79	2.391	(112)	30
2.169	68	2.168	(204),(310)	23
2.148	39	2.146	(013)	21
1.849	33	1.847	(41 $\bar{1}$)	16
1.818	54	1.817	(114)	17
1.535	60	1.535	(21 $\bar{5}$)	25

be related to the Mn-O vibrations perpendicular to the direction of the MnO₆ octahedral double chains. The Raman band at 574 (577, 583 in this paper) cm⁻¹ may correspond to the displacement of the oxygen atoms relative to the manganese atoms along the octahedral chains (Julien et al., 2003; Gao et al., 2008). The presence of Ag and other cations changes the relative intensities of these two bands in our samples which can be used to characterize the tunnel structure of cryptomelane. The low-frequency Raman bands at 183 (184) cm⁻¹ is assigned to an external vibration that derives from the translational motions of the MnO₆ octahedra; the Raman band at 380 (386) cm⁻¹ is ascribed to the Mn-O bending vibrations (Gao et al., 2008). These low-frequency bands show weaker in XG-C-2 than those in XG-C-1 because

Figure 5. Raman spectra of argentinean cryptomelane (XG-C-1 and XG-C-2), ranciéite, chalcophanite and coronadite.

higher concentration of Ag and Ca might change the vibrational interactions of O-Mn-O-Mn-O chains.

Although both of coronadite and cryptomelane attribute to hollandite species, the doping cations of K, Ag and Pb make the Mn-O stretching vibration and translational motion of MnO₆ octahedra different. The diagnostic high frequency bands combine into a broad peak centered at 595 cm⁻¹ in coronadite and the low frequency band at 185 cm⁻¹ becomes very weak. The cryptomelane also can be distinguished from ranciéite and chalcophanite having the layer structure by Raman spectrums. The important Raman change is observed on the symmetric stretching frequency (Mn-O) of MnO₆ groups at 645 and 651 cm⁻¹, which presents a shift of 15-20 cm⁻¹ towards the high-wavenumber side for the ranciéite and chalcophanite respectively in comparison with cryptomelane.

The band located at 606 cm⁻¹ might attribute to the Mn-O stretching vibration in the basal plane of [MnO₆] sheet in chalcophanite, but the disappearance of this band in ranciéite might suggest a softening of the Mn-O bond along the interlayer direction. Above all the local structure of manganese oxides with poor crystallinity are as a function of the nature of ions located in between the basal MnO₆ sheets or tunnel. The effect of the cation incorpo-

Table 4. Raman scattering data of manganese oxides in Xiangguang Mn-Ag deposit and references

Minerals			Wavenumbers (cm ⁻¹)								
Argentian Cryptomelane	183	273	380	509	577	628				This paper	
	184	279	386	509	583	630				This paper	
Cryptomelane	183	286	330	386	470	512	574	634	753	(Gao et al., 2008)	
	188	291		395	486	519	588	643	760	(Hernández et al., 2010)	
			321		467		571	(Kim and Stair, 2004)			
Coronadite	185	279	380		502	595				This paper	
		263	385			563				RRUFF database No. R060258	
		268	386	484		583				RRUFF database No. R070320	
	155	280	378	449	496	572				RRUFF database No. R090056	
Chalcophanite	163	273	384		502	606	651				This paper
			330	392	450	500	560	673	(Kim and Stair, 2004)		
							570	670	(Pitarch et al., 2014)		
		242	321	376	450	482	510	542	644	689	RRUFF database No. R050451
	175	219		385	484	512	570	669	RRUFF database No. R050605		
	177	219		388	485	512	569	670	RRUFF database No. R060271		
Ranciéite		301	370			645				This paper	

ration into the interlayer or tunnel space results in disordered Mn-O chemical bonds and change in the covalency of MnO₆ octahedra and a partial reduction of the Mn⁴⁺ ions which results in a modification of the vibrational mode frequencies that is inherent to the presence of low valence of Mn ions (Julien et al., 2003). However, an unequivocal assignment of some bands and the other weak bands is difficult in this stage, and these Raman modes reported here will be pursued in our succeeding studies.

Transmission electron microscopy

TEM study reveals well crystallized cryptomelane with plate-like sheets in XG-C-1, but tiny to amorphous grains in XG-C-2 (Figs. 6a and 7a). The interplanar distances of 6.92, 3.11 and 4.97 Å corresponds with (101), (301), (200) reflection of the cryptomelane phase respectively in XG-C-1 (Figs. 6b and 6c). Another argentian cryptomelane in XG-C-2 have characteristic interplanar distances of 6.9–7.0, 4.9 and 3.1–3.2 Å (Figs. 7c and 7d). The developed structural defects as lattice dislocations, distortions and stria combinations make the crystal fringes diverse (Figs. 6d and 7b).

DISCUSSION

Nanometric native silver has been reported to be adsorbed on todorokite at the San Miguel Tenango Mn-Ag mine (Gómez-Caballero et al., 2010), but it was not observed in argentian cryptomelane during our TEM and Raman

Figure 6. High resolution TEM image of argentian cryptomelane in the sample XG-C-1.

experiments. SEM-EDS maps also show the uniform distribution of silver in cryptomelane instead of local enrichment. So it is more probably for Ag cations to be accommodated into the atomic architectures rather than nanometric silver minerals to be adsorbed on the surface of cryptomelane.

The compositional and structural properties of cryptomelane have been studied in considerable detail by

Figure 7. High resolution TEM image of argentian cryptomelane in the sample XG-C-2.

many researchers (Bystörm and Bystörm, 1950; Post et al., 1982). It is a typical 2×2 tunnel structure manganese oxide, which is composed of edge-sharing double $[\text{MnO}_6]$ octahedral chains (Post et al., 1982; Lu et al., 2003). The substitution of Mn^{4+} by Mn^{3+} and/or Mn^{2+} in the framework can be balanced by the insertion of large monovalent cation—K within the tunnel (Pasero, 2005). The presence of potassium is necessary for the formation of cryptomelane to prevent the tunnel structure from collapsing. The two K positions per unit cell are only half filled, because the short K–K distance of 0.28 nm will make the structure unstable due to repulsive forces between the cations if all of the K sites are filled (Bystörm and Bystörm, 1950). The upper limit for potassium in cryptomelane is about 7 wt%, while the lower limit lies between 0.25 wt% and 2.2 wt%K (Burser et al., 1954; McKenzie, 1971).

Cryptomelane have several 2×2 tunnel structure analogues in nature. Barium, lead and sodium cations which have large radii similar to that of potassium can proxy for potassium as in the high-barium mineral hollandite, the plumbous mineral coronadite and the sodium-rich mineral manjiroite (Bystörm and Bystörm, 1950; Nambu and Tanida, 1967; Post and Bish, 1989). The states of oxidation of manganese partly determine what kind and how much mono- or divalent cations can enter the tunnels at the time the manganese minerals form (Gruner, 1943; Hildebrand and Mosier, 1974). Furthermore, silver, cesium, copper, nickel, lithium, cobalt, chromium-modified cryptomelane are reported to be synthesized successfully (Santos et al., 2009; Hernández et

Figure 8. Correlation plots of (a) $(\text{CaO} + \text{AgO} + \text{PbO})$ versus K_2O . (b) $(\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2)$ versus MnO_2 in argentian cryptomelane from Xiangguang deposit.

al., 2012; Özacar et al., 2013; Sun et al., 2014). These cations partially occupy locations within the tunnels to stabilize charge. In most cases minor distortions of the framework and/or ordered distributions of cations cause some deviation of the symmetry of these modified cryptomelane (Pasero, 2005).

The structure of cryptomelane allows considerable flexibility in chemical composition as a result not only of tunnel cation exchange, but also of octahedral framework replacements (Pasero, 2005). In nature the composition of cryptomelane also depends upon what elements are available in the solutions at the time of formation (Hildebrand and Mosier, 1974). For this reason, cryptomelane has a wide compositional variability of K, Ag, Ca, Pb, Al, Fe and Si contents in Xiangguang Mn–Ag deposit (Table 1). Regardless of those elements less than 1 wt%, elemental correlation plots of $(\text{AgO} + \text{PbO} + \text{CaO})$ concentrations vs K_2O concentrations and $(\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2)$ concentrations versus MnO_2 concentrations are shown in Figure 8. $(\text{AgO} + \text{PbO} + \text{CaO})$ contents show

well defined negative correlation trends with K_2O (Fig. 8a). The result illustrates the substitution relationship of mono- and divalent cations to potassium, which also means silver, calcium and lead probably occupy the tunnel sites in cryptomelane instead of potassium. The ionic radius and valence states are regarded as the most important factors that determine which cations can be stably doped in the tunnel of cryptomelane in natural conditions (Turner and Buseck, 1979; Post, 1999; Pasero, 2005). The radius of Ag^+ (1.26 Å) is adjacent to that of K^+ (1.33 Å) and Pb^{2+} (1.20 Å), but both silver and potassium are monovalent while lead is divalent. So it is more suitable for silver to enter the structure of cryptomelane involving substitution of potassium than coronadite involving substitution of lead. That explains why higher silver contents in cryptomelane than coronadite shown in Table 2. In addition, the elements of ($Fe_2O_3 + Al_2O_3 + SiO_2$) appear to negatively correlate with MnO_2 , but the trends are more scattered (Fig. 8b). It is possibly due to EMPA calculation contributing Mn^{2+} , Mn^{3+} to Mn^{4+} which results in higher MnO_2 content than the actual value. Trivalent aluminum, iron and tetravalent silicon could replace manganese in the $[MnO_6]$ octahedron shared by corners and/or edges, in comparison with, in general, SiO_4 - and AlO_6 - frameworks of the aluminosilicates.

Silver (1.2–3 wt%) and calcium (2–3 w%) contents are not sufficient to change the ratio of Mn vs other cations ($K + Ag + Ca \dots$) $\approx$ 8:1 in the cryptomelane compositions of XG-C-2, but some lattice distortions are caused by these substitutions. The Mn–O lattice vibrations within the MnO_6 octahedral double chains are weakened in Raman spectroscopy (Fig. 5). The substitutions of calcium together with silver might give a great effort to some lattice distortions including the configurations of variously sized tunnel structures and considerable positional disorders on the tunnel sites due to different valence state and smaller radius of Ca^{2+} (0.99 Å) in comparison of K^+ (1.33 Å). Furthermore, except the predominant tunnel positions, silver ions may present on the surface of the cryptomelane as well (Ravikumar et al., 1998). However, our observation is limited to the instrument conditions, so more advanced sample preparation method and aberration-corrected Z contrast imaging of this mineral to discover its detailed crystal structure will be done further.

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