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## Sulfur-containing particles emitted by concealed sulfide ore deposits: an unknown source of sulfur-containing particles in the atmosphere

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### Abstract

Sources of sulfur dioxide, sulfates, and organic sulfur compounds, such as fossil fuels, volcanic eruptions, and animal feeding operations, have attracted considerable attention. In this study, we collected particles carried by geogas flows ascending through

- soil, geogas flows above the soil that had passed through the soil, and geogas flows ascending through deep faults of concealed sulfide ore deposits and analyzed them using transmission electron microscopy. Numerous crystalline and amorphous sulfurcontaining particles or particle aggregations were found in the ascending geogas flows. In addition to S, the particles contained O, Ca, K, Mg, Fe, Na, Pb, Hg, Cu, Zn, As, Ti,
- Sr, Ba, Si, etc. Such particles are usually a few to several hundred nanometers in diameter with either regular or irregular morphology. The sulfur-containing particles originated from deep-seated weathering or faulting products of concealed sulfide ore deposits. The particles suspended in the ascending geogas flow migrated through faults from deep-seated sources to the atmosphere. This is a previously unknown source
- of the atmospheric particles. This paper reports, for the first time, the emission of sulfur-containing particles into the atmosphere from concealed sulfide ore deposits. The climatic and ecological influences of these sulfur-containing particles and particle aggregations should to be assessed.

### 1 Introduction

- Sources of sulfur oxides, sulfates, and organic sulfur compounds are diverse and associated with natural and anthropogenic activities. Known sources of sulfur are volatile sulfur compounds derived from animal feeding operations (Trabue et al., 2008), and aerobic decomposition of food waste (Wu et al., 2010), biogenic sulfur from rice paddies (Yang et al., 1996, 1998) and the Subantarctic and Antarctic Oceans (Berresheim, 1997).
- <sup>25</sup> 1987), sulfur gas (H<sub>2</sub>S and SO<sub>2</sub>) from geothermal fields (Kristmannsdottir et al., 2000), organic sulfur compounds from sediments and immature crude oil (Sinninghe Damsté



et al., 1988), sulfur oxides from the oxidation of fossil fuels (Soleimani et al., 2007), and sulfur dioxide from acid factories and volcanic eruptions (Wong, 1978; Sweeney et al., 2008). Sulfate particles, which are important anthropogenic aerosols and influencing climate (Pósfai et al., 1997; Williams et al., 2001), occur in mineral dust (Kiehl, 1999). Furthermore, volcanic activity is a major contributor of sulfur to the atmosphere (Zreda-Gostynska et al., 1993; Graf et al., 1998; Streets et al., 2000; Seino et al., 2004; Bhugwant et al., 2009; Bao et al., 2010; Gieré and Querol, 2010), particularly in countries such as Japan, Indonesia, Réunion Island, the Philippines, Iceland, Guatemala,

and New Zealand (Rose et al., 1986; Andres et al., 1993; Streets et al., 2000; Seino et al., 2004; Chenet et al., 2005; Bhugwant et al., 2009).

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Sulfur dioxide is retained in the stratosphere and subsequently concentrated by atmospheric processes, leading to adverse environmental consequences for plants, animals, and humans (Wong, 1978; Chenet et al., 2005). Existing research shows that  $SO_2$  is oxidized to  $SO_4^{2-}$  in both the gas and liquid phases. Moreover, sulfate aerosols can directly affect the climate (Graf et al., 1998). In our previous work, particles car-

- ried by an ascending geogas flow in the soil (Holub et al., 1999; Cao et al., 2009, 2010b, 2011; Liu et al., 2011; Wei et al., 2013) were studied and found to contain sulfur particles. Further research showed that sulfur-containing particles carried by ascending geogas flows can be transported through the soil layers and into the atmosphere.
- <sup>20</sup> Sulfur-containing particles suspended in the ascending geogas flow migrate through faults from deep-seated concealed sulfide ore deposits to the Earth's surface. These particles are a previously unknown source of sulfur-containing particles in the atmosphere. This paper reports, for the first time, the emission of sulfur-containing particles into the atmosphere from concealed sulfide ore deposits. Because concealed sulfide
- ore deposits are widely distributed, the influence of sulfur-containing particles derived from them is important. The climatic and ecological effects of these particles should be studied.



#### 2 Methods

Particles carried by an ascending geogas flow above the soil (that had flown through the soil), in the soil, and in deep-seated faults were collected at the Dongshengmiao polymetallic sulfide deposit in the Inner Mongolia Autonomous Region, China. Particles

- <sup>5</sup> carried by the ascending gas flow in the soil were also collected at other concealed ore deposits containing sulfide minerals, such as the Kafang copper deposit of the southern Yunnan Province, the Yongshengde copper deposit in northeastern Yunnan, and the Qingmingshan copper–nickel sulfide deposit in Guangxi Province, China.
- Particles transported by the ascending geogas flow above the soil (that had flown through the soil) were sampled using stainless steel tubes and carbon-coated nickel transmission electron microscopy (TEM) grids. The length of the stainless steel tubes was 40 cm and their diameter was 2.8 cm. These tubes were inserted vertically into the soil to a depth of about 30 cm. A carbon-coated nickel TEM grid was fixed at the end of the stainless steel tubes. The ascending geogas flow in the soil moved into the stain-
- <sup>15</sup> less steel tubes and naturally passed through the 30 cm soil layer. Then, the gas flow passed through the 10 cm of the empty stainless steel tubes above the soil. Finally, the geogas flow arrived at the top of the tubes. Particles carried by the geogas flow were adsorbed onto the carbon-coated nickel TEM grid. A protective device was installed on the outside of the steel tubes to ensure that particles sampled were those carried
- <sup>20</sup> by the ascending geogas flow. Sampling devices were installed between 25 July, and 23 August 2013, and the carbon-coated nickel TEM grids were retrieved on 8 September 2013. Sampling sites were distributed across a fault above the concealed sulfide ore bodies of the Dongshengmiao polymetallic sulfide deposit.

Particles transported by the ascending geogas flow in the soil were collected using an ordinary plastic funnels. An inverted funnel was inserted in a hole that was 60– 80 cm deep and backfilled with soil, and a TEM grid was fixed at the end of the funnel spout with nylon net. The setup was protected from contamination using plastic pipes and cups. The TEM grids were retrieved after 60 days.



Particles carried by ascending geogas flows in deep-seated faults were sampled using two methods. The first method used an active sampling device with a vacuum pump, polyvinyl chloride (PVC) pipe and carbon-coated nickel TEM grid as the main components. One end of the PVC pipe was connected with a tubing to the pump. A drilling steel was inserted slantwise into the fault. The inserted depth was 30–50 cm. As the drilling steel was pulled out, the PVC pipe was inserted into the hole. The PVC pipe was compacted using fault gouge. The impurity gases in the PVC pipe were pumped out using the vacuum pump, then, the PVC pipe was guickly sealed. A day later, we

- connected a tube equipped with a carbon-coated nickel TEM grid to the PVC pipe. The
   gas was pumped using a vacuum pump and flowed through the TEM grid for 1 to 2 h.
   Particles carried by the gas were collected by the TEM grid. Finally, the carbon-coated nickel TEM grid was removed and sealed in a sample cell. The second method did not use a vacuum pump. A carbon-coated nickel TEM grid was fixed to the end of the PVC pipe. The ascending geogas flow in the fault flowed into the PVC pipe and arrived at
- the top of the PVC pipe naturally. The particles carried by the geogas flows in the faults were adsorbed onto the carbon-coated nickel grid. The sampling devices were installed on 3–10 August 2013, and the TEM grids were retrieved on 7 September 2013. High-resolution TEM analyses were performed using a Tecnai G2 F30 S-TWIN instrument at Yangzhou University, China, using an accelerating voltage of 300 kV. The
- <sup>20</sup> grids were checked using TEM before sampling to ensure they were devoid of particles.

## 3 Results

# 3.1 Sulfur-containing particles carried by an ascending geogas flow above the soil (that had flown through the soil)

According to the TEM analysis, particles containing high levels of S, O, Pb, Zn, Fe, Hg,

As, etc, were found in the ascending gas flows above the soil above the Dongshengmiao polymetallic sulfide deposit. Table 1 provides the number of sulfur-containing par-



ticles or particle aggregations that were found on the  $100 \mu m \times 100 \mu m$  TEM grid. In general, one aggregation included more than five particles. Figure 1 shows an elliptical particle (ID: 1) having a diameter of 500 nm. The particle contains 78.17 % S and 18.47 % O (Table 2). Its O to S atomic ratio is 0.47. Figure 2 shows a particle aggregation (ID: 2) that consists of several small particles having a diameter of 3-8 nm. It contains 31.23 % S and 59.29 % Hg. The spacing of the lattice fringes was measured to be 0.333 nm. Figure 3 shows particle aggregations (ID: 3) with sizes of less than 100 nm. Their O to S atomic ratio is 0.51. The particle aggregations contain 14.48 % Pb. The particle (ID: 4) illustrated in Fig. 4 is elliptical with a diameter of 200 nm and contains 18.55% As, 54.2% Pb, and 8.34% Zn. The particle (ID: 5) shown in Fig. 5 10 contains 2.25% Co. It is amorphous and has an O to S atomic ratio of 2.91. The particle aggregation (ID: 6) illustrated in Fig. 6 contains 62.39 % Cu and consists of small particles each having a diameter of 5–10 nm. Figure 7 presents a particle aggregation (ID: 7) that consists of many small particles with diameters of about 5 nm, and contains 15 69.28 % Pb.

### 3.2 Sulfur-containing particles carried by an ascending gas flow in the soil

Numerous sulfur-containing particles transported by an ascending gas flow were found in the soil over sulfide ore deposits. Figure 8 shows an aggregation of such particles from the Dongshengmiao polymetallic sulfide deposit. The aggregation (ID: 8) may be composed of CaSO<sub>4</sub> with trace amounts of K, Mg, Fe, and Si. It is regularly shaped and 20 300 nm in size. The selected area electron diffraction pattern shows that the aggregation is polycrystalline. Figure 9 shows a TEM image of a sulfur-containing particle (ID: 9) from the Kafang copper deposit, South China. Sulfur accounts for 63.99% of the par-

ticle (Table 3), and its O to S atomic ratio is 0.83. Its K content is 8.93 %, and its size is 330 nm. Figure 10 shows a regularly polygonal particle (ID: 10) from the Yongshengde 25 copper deposit, China. Its O to S atomic ratio is 3.60, and its Fe and F contents are 9.94 and 1.71 %, respectively. Figure 11 shows a sulfur-containing particle (ID: 11) from the Qingmingshan Cu-Ni sulfide deposit, Guangxi Province, China. Its O to S atomic ratio



is 2.51. The particle contains 2.03 % Co and is 300 nm × 400 nm in size. The selected area electron diffraction pattern shows that the particle is amorphous.

## 3.3 Sulfur-containing particles carried by ascending geogas flows in deep-seated faults

- <sup>5</sup> Sulfur-containing particles were found in samples obtained using two methods from the deep fault gas of the Dongshengmiao polymetallic sulfide deposit. Figure 12 shows a sulfur-containing particle aggregation (ID: 12) that was obtained using the vacuum pump from the deep-seated fault gas near a concealed ore body. The aggregation contains O, Na, Si, S, K, Fe, Zn, and Pb. The S content is 23.8%. Figure 13 shows
   <sup>10</sup> a particle aggregation (ID: 13) that was obtaied using a PVC pipe from a fault near a concealed ore body. The ascending gas flow arrived at the top of the PVC pipe naturally, and the particles were adsorbed by a TEM nickel grid. The particle aggregation consists of many small particles that are 4–15 nm in diameter. The small particles are elliptical and crystalline, with 0.302 nm spacing of the lattice fringes, and and their main
   <sup>15</sup> components are O and S. Figure 14 shows a sulfur-containing particle (ID: 14) that was sampled using a PVC pipe in a fault above a concealed ore body. The vertical distance from the sample to the concealed ore body was 85 m. The vertical distance from the
  - sample to the Earth's surface was 230 m.

## 3.4 Sulfur-containing particles in deep-seated fault gouges and oxidized ores

<sup>20</sup> Sulfur-containing particles were also found in deep-seated fault gouges and oxidized zones of the Dongshengmiao polymetallic sulfide deposit. For example, Fig. 15 shows a sulfur-containing particle (ID: 15) from the oxidized zone. According to its atomic percentage – it contains SO<sub>4</sub><sup>2-</sup> and may be consist of Sr, Ba sulfate, and Ti oxide. Its size is 200 nm × 400 nm. Figure 16 shows a rhombus-shaped particle (ID: 16) from a deep-seated fault gouge. Its main components are O, S, and Ca, with minor amounts of Fe, Co, and Si.



Overall, the sulfur-containing particles or particle aggregations transported by ascending geogas flows can be both regular and irregular in shape and either crystalline or amorphous. The particles or particle aggregations contain Ca, K, Mg, Fe, Na, Pb, Hg, Cu, Zn, As, Ti, Sr, Ba, and Si, as well as O and S.

<sup>5</sup> The number of sulfur-containing particles in the ascending geogas flows in nonsulfur-rich areas is much lower than that from the sulfide ore deposits. Furthermore, the overwhelming majority of particles in non-sulfur-rich areas have a low sulphur content. These areas are different from those with the sulfide ore deposits, in which sulfur-containing particles are densely distributed and are present at high levels in the ascending geogas flows.

#### 4 Discussion and conclusions

Gold particles are formed by post-mineralization fault activity, oxidation, and bacterial weathering of primary minerals (Cao et al., 2010a). Deep-seated gold particles can be transported to the surface by an ascending gas flow, as Brownian motion enables the gold particles in the ascending gas flow to overcome the effect of gravity (Cao et al., 2010a; Cao, 2011). We assume that the same mechanism applies to sulfur-containing particles or particle aggregations. Primary sulfur-containing minerals are transformed into particles by epigenetic reworking, such as post-mineralization fault activity, in which S<sup>2-</sup> in the sulfide minerals is oxidized to S<sup>6+</sup>. In this study, the sulfur-containing particles from fault gouges and oxidation of ores. Faulting and oxidation are well-developed in the Dongshengmiao polymetallic sulfide deposit and other sulfide deposits. This finding indicates that faulting and oxidation play an important role in particle formation.

<sup>25</sup> Sulfur-containing particles may be transported to the surface by an ascending geogas flow through faults. Because gases and particles move along faults, they can migrate over long distances (Etiope and Martinelli, 2002; Cao et al., 2010a). Material



carried by an ascending geogas flow in the soil in the Xuanhan gas field, Sichuan Province, China was sampled and measured using an instrumental neutron activation analysis. Analysis of trace element anomalies has shown the gas-bearing ring fracture structure to be 4000 m deep, suggesting that particles carried by an ascending geogas

- flow can be transported over long distances (Yang et al., 2000). The gas flow migrates upward because of the temperature difference and the pressure differences between the Earth's interior and its surface is the reason that the gas flow migrate upward (Tong and Li, 1999; Etiope and Martinelli, 2002; Cao et al., 2010a). In this study, the particles or particle aggregations were found in ascending geogas flows in faults at different
- depths near or above the concealed ore bodies of the Dongshengmiao polymetallic sulfide deposit. This observation demonstrates that the faults are channels for particles carried by the ascending geogas flow. Sulfide-containing particles suspended in gas above the soil were found, showing that these particles can move through the soil and get into the atmosphere.
- The probability that these particles are transported by an ascending geogas flow originating in the soil is low. In the study area, the soil consists of kaolinite, halloysite, montmorillonite, illite, chlorite, hematite, quartz, goethite, and similar minerals. Kaolinite is the main mineral, and the sulfur content in the soil is low. Therefore, this soil is clearly not a probable source of sulfur-containing particles transported by an ascending
- 20 geogas flow. Furthermore, there is no correlation between the numbers of these particles and those of sulfur-containing particles in the soil solid phase. Sulfur-containing particles are clearly enriched in soils above deep sulfur-rich sources because sulfurcontaining particles transported by an ascending geogas flow were found in more than ten deep sulfide ore bodies that were studied. This result indicates a close relation-
- ship between sulfur-containing particles in the gas flow and deep-seated sulfide ore bodies. Other rock types, such as limestone, siltstone, sandstone, and mudstone, do not contain sufficient sulfur to become sources of sulfur-containing particles in an ascending gas flow; for example, the mean sulfur concentrations of the Devonian limestone, mudstone, siltstome, and sandstone in the northern Guangdong Province, China



are  $610 \times 10^{-6}$  (68 samples),  $80 \times 10^{-6}$  (25 samples),  $160 \times 10^{-6}$  (33 samples), and  $110 \times 10^{-6}$  sulfur (4 samples), respectively.

Concealed metal deposits containing sulfide minerals can be very extensive, such as the Killik massive sulfide deposit, northeastern Turkey (Çiftçi et al., 2005); and the Masa Valverde blind massive sulfide deposit, Spain (Ruiz et al., 2002); and the Huize carbonate-hosted Zn–Pb–(Ag) District, South China (Han et al., 2007). Thus, sulfur-containing particles could be widely distributed above many concealed sulfide ore deposits.

Such sulfur-containing particles enter the atmosphere. Several studies have discussed the direct effects of sulfate particles on the climate (Liu et al., 2009). Some researchers have suggested that sulfur-containing particles can reduce atmospheric temperature or result in climate warming. Ward (2009) reported that trace amounts of sulfuric acid aerosols influence climate change. All major historic volcanic eruptions have cooled the Earth's surface by approximately 0.5 °C for the succeeding three years.

- <sup>15</sup> Large volumes of sulfur dioxide released by frequent eruptions adversely affect the oxidizing capacity of the atmosphere resulting in very rapid warming. Streets et al. (2000) suggested that because sulfate aerosols play a vital role in cooling the atmosphere, a reduction in sulfur dioxide emissions in the future would result in increased global warming. Furthermore, aerosol sulfate has been identified as an important contributor
- <sup>20</sup> to sunlight scattering (Lelieveld and Heintzenberg, 1992; Kim et al., 2001). The mean negative radiative forcing by sulfates in the Northern Hemisphere alone has been estimated at  $-1.1 \text{ W m}^{-2}$  (Charlson et al., 1991; Kim et al., 2001). Niemeier et al. (2011) revealed that an increase in the SO<sub>2</sub> emission rate does not lead to a similar increase in radiative forcing because, as the size of the aerosols increases, their lifetime de-<sup>25</sup> creases. It is thus possible that the sulfur-containing particles transported by an as-

creases. It is thus possible that the sumi-containing particles transported by an ascending geogas flow have an effect on the climate and should, therefore, be evaluated.
 Sulfate particles can be transported into the lungs leading to respiratory illnesses (World Bank Group, 1999; Soleimani et al., 2007). In particular, the sulfur-containing particles containing high levels of toxic Pb, Hg, Cu, and As. The possible relationship



between the occurrence of sulfur-containing particles transported by an ascending geogas flow and endemic diseases in the vicinity of sulfur-containing deposits should be investigated.

It is probable that sulfur-containing particles transported by the ascending geogas flows in the soil affect the soil system; for example, sulfur-containing particles can affect both soil biota and enzymatic activities, resulting in changes in the soil structure, nutrient cycling, and organic matter decomposition and retention. Sulfur-containing particles may directly catalyze organic matter decomposition. Furthermore, the potential use of such particles as fertilizers for rice plants needs to be investigated.

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**Table 1.** Number of sulfur-containing particles or particle aggregations number from the Dong-shengmiao deposit on  $100 \,\mu$ m ×  $100 \,\mu$ m TEM grids.

Sulfur-containing particles or particle aggregations carried by ascending gas flow above the soil (that had flown through the soil)			Sulfur-c aggreg	ontaining parti jations carried gas flow in dee	cles or p by asce p faults	oarticle nding	
Sample	Sample box	Grid	Number	Sample	Sample box	Grid	Number
ND13-1	A1	A1-1	3	NDDW03	A2	A2-2	3
ND13-2	A2	A2-1	2	NDDW05	A4	A4-1	1
ND13-3	A3	A3-2	1			A4-2	29
		A3-3	6	NDDW06	A5	A5-2	1
ND13-4	A4	A4-1	1	NDDW07	B1	B1-1	4
		A4-2	2			B1-2	1
ND13-6	A5	A5-1	1	NDDW19	D3	D3-2	1
		A5-2	3			D3-3	2
		A5-3	1	NDDW26	E4	E4-1	1
ND13-8	B2	B2-1	1			E4-3	1
		B2-2	6	NDDW27	E5	E5-1	2
		B2-3	1			E5-3	2
ND13-9	B3	B3-1	1			E5-4	1
		B3-2	1	NDDW36	G4	G4-1	12
		B3-3	1			G4-3	10
ND13-10	B4	B4-1	1			G4-4	1
		B4-3	6	NDDW37	G5	G5-1	1
ND13-11	B5	B5-1	1				

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Element				Particle	number			
	1	2	3	4	5	6	7	8
Weight O %	18.47	9.46	16.02	9.73	15.75	12.9	5.13	51.88
Atomic O %	31.1	31.78	31.12	39.3	34.16	31.35	22.74	69.78
Weight Si %	3.35		1.49	0.5	1.09	3.08		2.19
Atomic Si %	3.21		1.65	1.15	1.34	4.27		1.67
Weight S %	78.17	31.23	63.1	3.82	10.83	21.61	18.25	19.02
Atomic S %	65.68	52.33	61.16	7.7	11.72	26.2	40.32	12.76
Weight Hg %		59.29						
Atomic Hg %		15.87						
Weight K %			4.88		35.75		7.31	0.99
Atomic K %			3.88		31.73		13.25	0.54
Weight Pb %			14.48	54.2	22.5		69.28	
Atomic Pb %			2.17	16.9	3.76		23.67	
Weight Na %				3.1	9.66			
Atomic Na %				8.73	14.58			
Weight Fe %				0.75	2.14			0.21
Atomic Fe %				0.87	1.33			0.08
Weight Co %				0.98	2.25			
Atomic Co %				1.08	1.32			
Weight Zn %				8.34				
Atomic Zn %				8.24				
Weight As %				18.55				
Atomic As %				16				
Weight Cu %						62.39		
Atomic Cu %						38.16		
Weight Mg %								3.86
Atomic Mg %								3.42
Weight Ca %								21.82
Atomic Ca %								11.71

#### **Table 2.** EDX results for particles 1–8.



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Table 3. EDX results for particles 9-16.

Element	Particle number							
	9	10	11	12	13	14	15	16
Weight O %	26.54	56.25	53.66	25.39	67.03	17.21	29.21	40.8
Atomic O %	42.51	73.54	70.2	37.32	80.72	35.83	64.85	62.97
Weight Si %	0.52			0.66	1	0.7		1.5
Atomic Si %	0.47			0.55	0.68	0.83		1.32
Weight S %	63.99	31.3	42.81	23.8	28.01	24.59	10.88	15.03
Atomic S %	51.15	20.42	27.95	17.45	16.83	25.53	12.05	11.58
Weight K %	8.93	0.78		2.01	2.59			
Atomic K %	5.85	0.42		1.21	1.27			
Weight Pb %				4.25				
Atomic Pb %				0.48				
Weight Na %			1.04	40.92		1.35		
Atomic Na %			0.95	41.84		1.96		
Weight Fe %		9.94	0.44	1.11	1.35	51.16	1.27	5.2
Atomic Fe %		3.72	0.16	0.46	0.46	30.5	0.81	2.3
Weight Co %			2.03					6.36
Atomic Co %			0.72					2.66
Weight Zn %				1.82				
Atomic Zn %				0.65				
Weight Mg %						2.74		
Atomic Mg %						3.75		
Weight Ca %						0.28	0.5	31.08
Atomic Ca %						0.23	0.44	19.15
Weight F %		1.71						
Atomic F %		1.88						
Weight Al %						0.25		
Atomic Al %						0.3		
Weight Mn %						1.68		
Atomic Mn %						1.02		
Weight Ti %							10.94	
Atomic Ti %							8.11	
Weight Sr %							10.32	
Atomic Sr %							4.18	
Weight Ba %							36.86	
Atomic Ba %							9.53	





**Figure 1.** TEM image of an S-, O-, and Si-containing particle obtained from an ascending gas flow above the soil over the Dongshengmiao deposit.





**Figure 2. (a)** TEM image, **(b, c)** high-resolution (HRTEM) images, and **(d)** selected area electron diffraction (SAED) pattern of an S-, O-, Hg-containing particle aggregation obtained from an ascending gas flow above the soil over the Dongshengmiao deposit.





**Figure 3.** TEM image of S-, O-, K-, and Pb-containing particle aggregations obtained from an ascending gas flow above the soil over the Dongshengmiao deposit.





ascending gas flow above the soil over the Dongshengmiao deposit.



Figure 5. (a) TEM image and (b) SAED pattern of an S-, O-, K-, Na-, and Pb-containing particle obtained from an ascending gas flow above the soil over the Dongshengmiao deposit.

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Figure 6. (a) TEM image and (b) HRTEM image of an O-, Si-, S-, and Cu-containing particle aggregation obtained from an ascending gas flow above the soil over the Dongshengmiao deposit.





Figure 7. (a) TEM image, (b) HRTEM image, and (c) SAED pattern of an O-, S-, K-, and Pbcontaining particle aggregation obtained from an ascending gas flow above the soil over the Dongshengmiao deposit.











**Figure 9.** TEM image of an O-, S-, and K-containing particle obtained from an ascending gas flow in the soil from the Kafang copper deposit, Yunnan Province.





**Figure 10.** TEM image of an O-, S-, and Fe-containing particle obtained from an ascending gas flow in the soil from the Yongshengde copper deposit in northeastern Yunnan.



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**Figure 11. (a)** TEM image and **(b)** SAED pattern of an O-, S-, and Co-containing particle obtained from an ascending gas flow in the soil from the Qingmingshan Cu–Ni sulfide deposit, Guangxi Province.





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**Figure 12.** TEM image of an O-, S-, K-, Pb-, and Na-containing particle sampled using a vacuum pump from the fault gas near a concealed ore body of the Dongshengmiao deposit.



**Figure 13. (a)** TEM image, **(b, c)** HRTEM images, and **(d)** SAED pattern of an O-, S-, and K-containing particle aggregation sampled using a PVC pipe in a fault near a concealed ore body of the Dongshengmiao deposit.





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**Figure 14.** TEM image of an O-, S-, Fe-, and Mg-containing particle aggregation sampled using a PVC pipe in a fault above a concealed ore body of the Dongshengmiao deposit.



Figure 15. TEM image of an O-, S-, Ti-, Sr-, and Ba-containing particle from a deep-seated oxidized zone in the Dongshengmiao deposit.





**Figure 16.** TEM image of an O-, S-, Fe-, Co-, and Ca-containing particle from a deep-seated fault gouge in the Dongshengmiao deposit.