

Supplement of Atmos. Chem. Phys., 15, 6959–6969, 2015  
<http://www.atmos-chem-phys.net/15/6959/2015/>  
doi:10.5194/acp-15-6959-2015-supplement  
© Author(s) 2015. CC Attribution 3.0 License.



Atmospheric  
Chemistry  
and Physics  
Open Access

The logo for the journal Atmospheric Chemistry and Physics, featuring the letters 'EG' inside a circle with a crosshair.

*Supplement of*

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

**J. J. Cao et al.**

*Correspondence to:* J. J. Cao (eescjj@mail.sysu.edu.cn)

The copyright of individual parts of the supplement might differ from the CC-BY 3.0 licence.

## Supplementary Information

For 16 ore deposits, in which we have studied particles carried by ascending geogas, a large number of sulfur-containing and Pb- and As-containing particles were found. There are oxidative ore bodies in many concealed sulfide ore deposits. As sulfide minerals change into oxide minerals, sulfide was released from these minerals. There are some sulfide concentration data for ascending geogas. Yuan et al. (China University of Geosciences, Beijing, China, 2014) analyzed sulfide concentrations of ascending geogas in soil at the Sunit deposit (the Inner Mongolia Autonomous Region, China), using plasma mass spectrographic analysis. Their sampling method allowed the flow of geogas in the soil through liquid collector slowly using a pump. The particles carried by the ascending geogas flow were adsorbed in the liquid collector. The volume of the geogas extracted per hole was 5 liters. The geogas extracted from 3 holes (15 liters) was combined to make one sample. The liquid collector was made with high purity nitric acid and Mini-Q ultra pure water. The liquid collector was placed in a 25 ml polyethylene bottle. The analysis results from 1054 samples showed that the average sulfur content of the liquid collector was  $26.4571 \mu\text{g ml}^{-1}$ . The maximum value was  $35.33 \mu\text{g ml}^{-1}$  and the minimum value was  $16.89 \mu\text{g ml}^{-1}$ . A concentration of  $26.4571 \mu\text{g ml}^{-1}$  in the liquid collector may be translated into 44.095 mg per cubic meter of geogas flow. We know that sulfur-containing substances carried by geogas flow may be not completely adsorbed in the liquid collector. Therefore, the average sulfur content of the ascending geogas flow may have been higher than 44.095 mg per cubic meter. We analyzed the sulfide concentration of

ascending geogas in the soil at the Kangjiawan deposit in the Hunan Province, China. Our sampling method is similarly to the method used by Yuan et al. (2014). The main difference is that our liquid collector was made with high purity aqua regia and tri-distilled water. The volume of the liquid collector was 100 ml. The volume of the geogas extracted from a hole was 9 liters. Therefore, the volume of the geogas extracted from 3 holes was 27 liters. The sulfide concentration of the liquid collector was analyzed using the plasma spectrum method. We analyzed the samples along 3 sections (sample numbers were 31, 74, and 20). The results showed that the average sulfur contents of the 3 sections were 0.27, 1.40, and 32.81  $\mu\text{g ml}^{-1}$  respectively (Tables S1–3), which may be translated into 1.00, 5.19, and 121.50 mg per cubic meter of geogas flow, respectively. Wang et al. (2008) collected particles carried by ascending geogas in soil over the Jiaolongzhang Pb-Zn-Cu-Ag deposit, Eastern Gansu, China using a liquid collector. Analysis results from 14 samples showed that the mean content of Cu, Pb, and Zn was 844 ng/ml (gas volume), 107 ng/ml, and 1751 ng/ml, respectively.

There is earth degassing phenomena in metallic and nonmetallic deposits. The giant gold deposits, such as the Porcupine gold deposit in Canada, the Witwatersrand gold deposit in South Africa, and the Muruntau gold deposit in Uzbekistan, exhibit upward vertical movement of hydrocarbon gas. The Witwatersrand gold deposit has significant upward gas flow. In one day, 36700  $\text{m}^3$  of hydrocarbon gases degas from underground gold mining vents and  $5 \times 10^8 \text{ m}^3$  of hydrocarbon gases degas from 3000m or deeper mines every year. The Azerbaijan oil and gas region is strongly

degassed, with  $4 \times 10^8 \text{ m}^3$  of gases degassed every year (Du, 2009). The ascending gas flow rates were measured to be between  $60 \times 10^{-4}$  and  $4 \text{ cm}^3 \text{ min}^{-1} \text{ m}^{-2}$  horizontally projected borehole area at three different sites by Malmqvist & Kristiansson (1984). Carbon dioxide concentrations above sulfide mineralizations are often enhanced. Hidden sulfide mineralizations at a depth of 200 m have been located in quartzite in areas such as Brittany, and sulphide ores have been located in granite in Cornwall. Above mineralizations, carbon dioxide in the soil gas has been found to increase to 10% from the normal concentration of 1%. The carbon dioxide flow may be as large as  $0.2 \text{ l m}^{-2} \text{ h}^{-1}$  (Hermansson et al. 1991). The Dongshengmiao deposit lies in a seismically active zone. The Langshan Mountain-front fault, in which minor earthquake activity frequently takes place and where M=6 earthquakes have taken place three times in the twentieth century, passes through the deposit. The release of geogas in active tectonic areas is widespread and occurs at a significant level (Judd et al., 1997; Etiope, 1999; Mörner and Etiope, 2002). The CO<sub>2</sub> emission flux of the Siena Graben Faults (Italy), Siena G. Arbia Fault (Italy), Ustica Arso Fault (Italy), and San Andreas Fault (California) were 0.83–1123, 12.4–74.4, 77.3, and 0.4–23 kg m<sup>-2</sup> year<sup>-1</sup> respectively (Etiope, 1995; 1999; Mörner and Etiope, 2002; Lewicki and Brantley, 2000). These equate, respectively, to 0.02–26.94, 0.3–1.78, 1.85, and 0.01–0.55 cm<sup>3</sup> m<sup>-2</sup> s<sup>-1</sup> if CO<sub>2</sub> density is assumed to be 1.3401 kg m<sup>-3</sup>. The area of the Dongshengmiao deposit is 4.65 km<sup>2</sup>. The emission flux estimation of the Dongshengmiao deposit was 0.5 cm<sup>3</sup> m<sup>-2</sup> s<sup>-1</sup> according to the emission fluxes of the above-mentioned faults and deposits. Therefore, the estimated degassing rate for the

Dongshengmiao deposit was  $2.325 \text{ m}^3 \text{ s}^{-1}$ .

The distribution areas of concealed sulfur ore deposits are different. The ore deposits with the distribution areas of 1–12  $\text{km}^2$  may have more deposits than other areas. Concealed metal deposits containing sulfide minerals can be very extensive, such as the Killik massive sulfide deposit in northeastern Turkey (Çiftçi et al., 2005), the Masa Valverde blind massive sulfide deposit in Spain (Ruiz et al., 2002), and the Huize carbonate-hosted Zn–Pb–(Ag) District in South China (Han et al., 2007). Concealed sulfur nonmetallic deposits, such as gypsum and barite, are also widely distributed. The number of concealed sulfide deposits is far greater than those of active volcanoes. Under the climate-warming conditions, oxidation of sulfur-containing minerals is particularly accelerated.

Table S1 Plasma spectrum S results for liquid collectors along the 1<sup>st</sup> section ( $\mu\text{g/mL}$ )

Number	S	Number	S	Number	S	Number	S
K1-1	0.22	K1-9	0.08	K1-17	0.12	K1-25	0.43
K1-2	0.20	K1-10	0.18	K1-18	0.13	K1-26	0.33
K1-3	0.13	K1-11	0.15	K1-19	0.26	K1-27	0.83
K1-4	0.12	K1-12	0.12	K1-20	0.27	K1-28	0.15
K1-5	0.12	K1-13	0.75	K1-21	0.68	K1-29	0.48
K1-6	0.12	K1-14	0.13	K1-22	0.37	K1-30	0.09
K1-7	0.35	K1-15	0.14	K1-23	0.91	K1-31	0.09
K1-8	0.13	K1-16	0.20	K1-24	0.11		

Table S2 Plasma spectrum S results for liquid collectors along the 2<sup>nd</sup> section (µg/mL)

Number	S	Number	S	Number	S	Number	S
K2-1	1.74	K2-20	3.81	K2-39	0.6	K2-58	0.31
K2-2	1.21	K2-21	1.52	K2-40	0.9	K2-59	0.58
K2-3	1.46	K2-22	4.44	K2-41	1.08	K2-60	0.42
K2-4	0.27	K2-23	0.72	K2-42	0.26	K2-61	0.59
K2-5	1.68	K2-24	1.07	K2-43	2.03	K2-62	3.86
K2-6	0.97	K2-25	0.57	K2-44	1.05	K2-63	0.51
K2-7	0.31	K2-26	0.43	K2-45	0.48	K2-64	0.57
K2-8	1.35	K2-27	0.61	K2-46	2.46	K2-65	0.2
K2-9	0.93	K2-28	0.11	K2-47	0.45	K2-66	0.2
K2-10	1.51	K2-29	0.39	K2-48	0.8	K2-67	0.49
K2-11	0.27	K2-30	1.39	K2-49	0.28	K2-68	0.29
K2-12	0.52	K2-31	0.88	K2-50	0.24	K2-69	0.87
K2-13	2.55	K2-32	0.6	K2-51	4.73	K2-70	0.65
K2-14	0.48	K2-33	4.63	K2-52	0.29	K2-71	0.3
K2-15	1.97	K2-34	1.84	K2-53	6.85	K2-72	8.28
K2-16	1.21	K2-35	4.1	K2-54	0.57	K2-73	0.48
K2-17	2.73	K2-36	1.92	K2-55	0.69	K2-74	1.84
K2-18	1.27	K2-37	1.18	K2-56	5.85		
K2-19	0.22	K2-38	0.38	K2-57	0.61		

Table S3 Plasma spectrum S results for liquid collectors along the 3<sup>rd</sup> section (µg/mL)

Number	S	Number	S	Number	S	Number	S
K3-1	34.90	K3-6	19.43	K3-11	4.08	K3-16	76.28
K3-2	2.35	K3-7	1.00	K3-12	16.88	K3-17	77.21
K3-3	4.89	K3-8	1.38	K3-13	74.51	K3-18	79.81
K3-4	0.52	K3-9	1.43	K3-14	51.57	K3-19	81.52
K3-5	2.65	K3-10	0.10	K3-15	49.66	K3-20	76.07

## References

- Çiftçi, E., Kolaylı, H., and Tokel, S.: Lead-arsenic soil geochemical study as an exploration guide over the Killik volcanogenic massive sulfide deposit, Northeastern Turkey, *J. Geochem. Explor.*, 86, 49–59, 2005.
- Du, L. T.: The new implication about oil-gas origin and outgassing of the earth obtained in Russia, Ukraine, Azerbaijan in new century, *Lithologic Reservoirs*, 21(4), 1–9, 2009 (in Chinese with English abstract).
- Etioppe, G.: Migrazione e comportamento del “Geogas” in bacini argillosi. Ph.D. Thesis, Dept. Earth Sciences, University of Rome “La Sapienza”, Extended abstract in *Plinius* (1996), 15, 90–94, 1995.
- Etioppe, G.: Subsoil CO<sub>2</sub> and CH<sub>4</sub>, and their advective transfer from faulted grassland to the atmosphere, *J. Geophys. Res.*, 104 (D14), 16889–16894, 1999.
- Han, R. S., Liu, C. Q., Huang, Z. L., Chen, J., Ma, D. Y., Lei, L., and Ma, G. S.: Geological features and origin of the Huize carbonate-hosted Zn–Pb–(Ag) District, Yunnan, South China, *Ore Geol. Rev.*, 31, 360–383, 2007.
- Hermansson, H. P., Akerblom, G., Chyssler, J., and Linden, A.: Geogas: A Carrier or a Tracer. SKN Report No. 51. National Board for Spent Nuclear Fuel, Stockholm, 1–66, 1991.
- Judd, A. G., Davies, J., Wilson, J., Holmes, R., Baron, G., and Bryden, I.: Contributions to atmospheric methane by natural seepages on the UK continental shelf, *Mar. Geol.*, 137, 165–189, 1997.
- Lewicki, J., and Brantley, S. L.: CO<sub>2</sub> degassing along the San Andreas fault, Parkfield,

California, *Geophys. Res. Lett.* 27, 5–8, 2000.

Malmqvist, L. and Kristiansson, K.: Experimental evidence for an ascending micro-flow of geogas in the ground, *Earth Planet. Sc. Lett.*, 70, 407–423, 1984.

Mörner, N.-A. and Etiope, G.: Carbon degassing from the lithosphere, *Global Planet. Change*, 33, 185–203, 2002.

Ruiz, C., Arribas, A., and Arribas, Jr., A.: Mineralogy and geochemistry of the Masa Valverde blind massive sulphide deposit, Iberian Pyrite Belt (Spain), *Ore Geol. Rev.*, 19, 1–22, 2002.

Yuan, L. L., Wang, M. Q., and Hu, J. L.: Research of geochemical gas prospecting in sunit, *Coal Technology*, 33, 85–87, 2014 (in Chinese with English abstract).

Wang, M. Q., Gao, Y. Y., and Liu, Y. H.: Progress in the collection of Geogas in China, *Geochem.: Explor. Environ. Anal.*, 8, 183–190, 2008.