S1 Sample pretreatment

In our work, sample pretreatment was conducted in a class 100 ultra-clean laboratory at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, and primarily included the preparation of PFA beakers and Teflon jars, sample digestion, and chemical purification.

S1.1 Preparation of PFA beakers and Teflon jars

To minimize background, the following protocol was used to clean PFA beakers (7 and 14 mL): 1) PFA beakers were wiped with ethanol-soaked swabs, and then immersed for 12 h in water which contained 1% detergent; 2) lint-free cotton was used to wipe the inner and outer walls of PFA beakers, which were then rinsed thoroughly with ultrapure water; 3) PFA beakers were sequentially soaked in 6 mol/L HNO_3 (120°C, 6 h), 4 mol/L HCl (120°C, 6 h), and ultrapure water (120°C, 6 h); 4) each PFA beaker was filled with 8 mol/L HNO_3 (5 mL) and heated at 120°C for 4 d with the lid closed, and after that the solution was discarded. After each of the above steps, PFA beakers were rinsed thoroughly with ultrapure water. Finally, PFA beakers were dried and stored for further usage.

Teflon jars (40 mL) used in digestion were cleaned using the procedure detailed in our previous work (Zhang et al., 2022; Zhang et al., 2023), and a brief overview is provided below. Each Teflon jaw was first rinsed three times with ultrapure water, and then cleaned using the following protocol: 1) it was filled with 2 mL ultrapure water and 4 mL concentrated HCl (guaranteed reagent), heated at 180°C for 1 h in a microwave digestion apparatus, and rinsed three times with ultrapure water; 2) it was filled with 2 mL ultrapure water and 4 mL HNO_3 (guaranteed reagent), heated at 180°C for 1 h in a microwave digestion apparatus, and rinsed

three times with ultrapure water; 3) it was filled with 1 mL ultrapure water and 3 mL HNO_3 (spectral grade), heated at 180°C for 1 h in a microwave digestion apparatus, and rinsed three times with ultrapure water. After being dried, Teflon jars were stored in clean zip-lock bags for further use.

S1.2 Sample digestion

S1.2.1 Desert dust, coal fly ash, municipal incineration fly ash, heavy fuel oil bottom ash, and urban particulate matter samples

The following procedure was employed to digest desert dust, coal fly ash, municipal incineration fly ash, heavy fuel oil bottom ash, and urban particulate matter samples.

1) The PFA beaker which contained a sample to be digested was filled with 2 mL HNO_3 (8 mol/L) and 1 mL HF (24 mol/L), heated at 120 °C for 7 days with the lid closed; after that, the lid was removed and the solution was evaporated to dryness.

2) The beaker was first filled with 0.5 mL H_2O_2 (10 mol/L), and after 30 min with 1.5 mL concentrated HNO_3; it was then heated at 120 °C for 1 h with the lid closed; after that, the lid was removed and the solution was evaporated to dryness.

3) It was filled with 4 mL of Aqua Regia and heated at 120 °C for 4 h with the lid closed; after that, the lid was removed and the solution was evaporated to dryness.

4) The PFA beaker was filled with 1.5 mL HCl (6 mol/L) and heated at 120 °C for 1 h with the lid closed; after that, the lid was removed and the solution was evaporated to dryness.

5) The PFA beaker was filled with 1 mL HCl (2.5 mol/L) and heated at 120 °C for 2 h with the lid closed until the solution became clear, and the obtained solution was transferred to a centrifuge tube for further experiments.

S1.2.2 Steelwork fly ash and biofuel burning aerosol

The following procedure was employed to steelwork fly ash and biofuel burning aerosol samples.

1) The Teflon jar which contained a sample to be digested was filled with 4 mL concentrated HNO_3 and 2.5 mL H_2O_2 (10 mol/L), and the beaker was kept at room temperature for 15 h.

2) It was filled with 5 mL concentrated HNO_3 and 2 mL HF (24 mol/L), and then digested at 180 °C for 3 h in a microwave digestion apparatus.

3) The Teflon jar was filled with 6 mL Aqua Regia and heated at 180 °C for 1 h with the lid closed; after that, the lid was removed and the solution was evaporated to dryness.

4) It was filled with 1.5 mL HCl (6 mol/L) and heated at 120 °C for 1 h with the lid closed; after that, the lid was removed and the solution was evaporated to dryness.

5) The Teflon jar was filled with 1 mL HCl (2.5 mol/L), heated at 120 °C for 2 h with the lid closed until the solution became clear. The solution was then transferred to a centrifuge tube and centrifuged at 5000 r/min for 3 min; and the obtained solution was used in chemical purification.

S1.3 Chemical purification

This study employed resin columns packed with 200-400 mesh AGMP-50 resin (Bio-Rad, USA) for chemical purification of Fe in all the solutions. The Eichrom polypropylene columns we used are 80 mm in height and ~8 mm in diameter, with resin bed volume of ~1 mL.

The entire purification procedure consists of five steps (Table S1), as detailed below. A reagent should only be introduced into the column after the previous one was completely drained from the resin column.

1) The resin column was sequentially filled with 10 mL HNO_3 (6 mol/L), 15 mL HCl (6 mol/L), and 5 mL of Milli-Q water to condition the resin, and the volume of each solution was 5 mL.

2) The resin column was filled with 1 mL HCl (0.2 mol/L HCl) to equilibrate the resin environment.

3) The resin column was filled with 100 μL sample solution which contained 80-210 μg Fe.

4) The resin column was sequentially filled with 1 mL HCl-HF mixed solution (both being 0.2 mol/L), 2 mL HCl-HF mixed solution (both being 0.2 mol/L), and then 1 mL HCl-HF mixed solution (with HCl and HF being 0.2 and 0.5 mol/L), in order to elute other elements contained by the sample solution.

5) The resin column was sequentially filled with 2 mL HCl-HF mixed solution (with HCl and HF being 0.2 and 0.5 mol/L) for three times, and then 1 mL of the same HCl-HF mixed solution. A PFA beaker was used to collect the eluate。

The beaker which contained the eluate was placed on a hotplate to evaporate the solution to dryness at 100 °C; after that, the beaker was filled with 200 μL concentrated HNO_3, and then placed on a hotplate to evaporate the solution to dryness at 120 °C. Finally, the beaker was filled with 1 mL HNO_3 (2% v/v) to dissolve the sample, and then placed on a hotplate at 100 °C

for 3 h with the lid closed. The resulting solution was used for Fe isotopic analysis by mass spectrometry.

Table S1. Fe purification procedure using the AGMP-50 resin.

Steps	Eluents	Volume/mL
Column cleaning	6 mol/L HNO_3	10
	6 mol/L HCl	15
	Milli-Q water	5
Conditioning	0.2 mol/L HCl	1
Sample loading	2.5 mol/L HCl	0.1
Matrix rinsing	0.2 mol/L HCl＋0.2 mol/L HF	3
	0.2 mol/L HCl＋0.5 mol/L HF	1
Fe collecting	0.2 mol/L HCl＋0.5 mol/L HF	7

S2 Experimental results

Table S2. Summary of δ^{56}Fe values (2σ) determined in our replicate measurements. The second column presents δ^{56}Fe values determined in individual measurements, and the third column presents the range of δ^{56}Fe values reported for replicate measurements (defined as the difference between the maximum and minimum values).

Sample	δ^{56}Fe (‰)	range (‰)
BCR-2	+0.07±0.07	0.04
	+0.13±0.14	
SARM4	+0.04±0.05	0.06
	+0.10±0.13	
Arizona test dust	+0.07±0.13	0.07
	+0.00±0.02	
	+0.05±0.01	
Luochuan loess	+0.15±0.13	0.02
	+0.13±0.13	
CFA-Chongqing	+0.50±0.14	0.08
	+0.58±0.13	
CFA-Neimenggu	-0.19±0.03	0.02
	-0.21±0.14	
Sintering Fly Ash-1	+0.15±0.03	0.07
	+0.08±0.02	
Peanut straw	-0.46±0.02	0.03
	-0.49±0.02	
municipal waste fly ash-FDU	+0.34±0.14	0.04
	+0.30±0.14	

Table S3. Summary of $\delta^{56}Fe$ (2σ) measured in our work for power plant coal fly ash samples (N: the number of measurements).

Sample	$\delta^{56}Fe$ (‰)	N	Note
CFA-Anhui	+0.33±0.13	1	This work
CFA-Chongqing	+0.54±0.11	2	This work
CFA-Fujian	+0.46±0.13	1	This work
CFA-Gansu	+0.47±0.13	1	This work
CFA-Guangdong-1	+0.33±0.13	1	This work
CFA-Guangdong-2	+0.57±0.13	1	This work
CFA-Guangxi	-0.02±0.13	1	This work
CFA-Guizhou	+0.00±0.13	1	This work
CFA-Hainan	+0.26±0.13	1	This work
CFA-Hebei	+0.24±0.13	1	This work
CFA-Heilongjiang	+0.03±0.13	1	This work
CFA-Henan	+0.30±0.13	1	This work
CFA-Hubei	+0.26±0.13	1	This work
CFA-Hunan	+0.16±0.13	1	This work
CFA-Jiangsu	+0.33±0.13	1	This work
CFA-Jiangxi	+0.28±0.13	1	This work
CFA-Jilin	+0.13±0.13	1	This work
CFA-Liaoning	+0.32±0.13	1	This work
CFA-Neimeng	-0.20±0.03	2	This work
CFA-Ningxia	+0.12±0.13	1	This work
CFA-Qinghai	+0.13±0.13	1	This work
CFA-Shaanxi	+0.29±0.13	1	This work
CFA-Shandong	+0.15±0.13	1	This work
CFA-Shanghai	+0.52±0.13	1	This work
CFA-Shanxi	+0.41±0.13	1	This work
CFA-Sichuan	+0.36±0.13	1	This work
GBW08401	+0.27±0.20	2	This work
CFA-FDU	+0.26±0.13	1	This work
CFA 2689	+0.05±0.08	1	(Li et al., 2022)
CFA 2691	+0.75±0.01	1	(Li et al., 2022)

Table S4. Summary of $\delta^{56}Fe$ (2σ) measured in our work for steelwork fly ash samples (N: the number of measurements).

Sample	$\delta^{56}Fe$ (‰)	N
Coking Fly Ash-1	+0.43±0.05	1
Coking Fly Ash-2	+0.42±0.00	1
Coking Fly Ash-3	+0.39±0.03	1
Sintering Fly Ash-1	+0.11±0.09	2
Sintering Fly Ash-2	+0.20±0.07	1
Sintering Fly Ash-3	+0.05±0.05	1
Sintering Fly Ash-4	+0.01±0.08	1
Sintering Fly Ash-5	+0.18±0.01	1
Blast Furnace Fly Ash-1	+0.12±0.07	1
Blast Furnace Fly Ash-2	+0.19±0.04	1
Converter Fly Ash-1	-1.11±0.02	1
Converter Fly Ash-2	+0.01±0.04	1
Post-S、steelmaking Fly Ash	-0.13±0.01	1
Casting Fly Ash	+0.02±0.02	1
Steelwork Emission Fly Ash-1	+0.09±0.02	1
Steelwork Emission Fly Ash -2	+0.20±0.05	1
Steelwork Emission Fly Ash -3	-0.02±0.03	1
Steelwork Emission Fly Ash -4	-1.16±0.03	1
Steelwork Emission Fly Ash -5	-0.38±0.04	1
Steelwork Emission Fly Ash -6	+0.29±0.00	1
Steelwork Emission Fly Ash -7	+0.02±0.13	1

Table S5. Summary of $\delta^{56}Fe$ (2σ) measured in our work for biofuel burning aerosol samples (N: the number of measurements).

Sample	$\delta^{56}Fe$ (‰)	N
Wheat straw	-0.15±0.01	1
Corn straw	-0.65±0.09	1
Peanut straw	-0.47±0.04	2
Soybean straw	+0.21±0.01	1
Rice straw	-0.18±0.04	1
Fir	+0.09±0.04	1
Birch	-0.35±0.04	1
Pine	-0.13±0.08	1
Lychee wood	+0.13±0.01	1
Apple wood	+0.03±0.02	1
Pear wood	-1.23±0.03	1

References

Li, R., Zhang, H., Wang, F., He, Y., Huang, C., Luo, L., Dong, S., Jia, X., and Tang, M.: Mass fractions, solubility, speciation and isotopic compositions of iron in coal and municipal waste fly ash, Sci. Total Environ., 838, 155974, 10.1016/j.scitotenv.2022.155974, 2022.

Zhang, H., Li, R., Dong, S., Wang, F., Zhu, Y., Meng, H., Huang, C., Ren, Y., Wang, X., Hu, X., Li, T., Peng, C., Zhang, G., Xue, L., Wang, X., and Tang, M.: Abundance and Fractional Solubility of Aerosol Iron During Winter at a Coastal City in Northern China: Similarities and Contrasts Between Fine and Coarse Particles, J. Geophys. Res. Atmos., 127, e2021JD036070, 10.1029/2021jd036070, 2022.

Zhang, H., Li, R., Huang, C., Li, X., Dong, S., Wang, F., Li, T., Chen, Y., Zhang, G., Ren, Y., Chen, Q., Huang, R., Chen, S., Xue, T., Wang, X., and Tang, M.: Seasonal variation of aerosol iron solubility in coarse and fine particles at an inland city in northwestern China, Atmos. Chem. Phys., 23, 3543-3559, 10.5194/acp-23-3543-2023, 2023.