

# Characteristics of trace metals in marine aerosols and their source identification over the Southern Ocean

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**Abstract** Atmospheric trace metals (Cu, Zn, Cd, Pb, Fe, V, and Cr), As, Al and Na in marine aerosols were studied over the Southern Ocean during the 28th Chinese National Antarctic Research Expedition. Fe was the most abundant of the analyzed trace metals, with an average concentration of  $28.824 \text{ ng}\cdot\text{m}^{-3}$ . V and Zn concentrations were also high, and their average concentrations were  $5.541 \text{ ng}\cdot\text{m}^{-3}$  and  $2.584 \text{ ng}\cdot\text{m}^{-3}$ , respectively. Although sea spray significantly influenced the marine aerosol particles measured (Na had the highest concentrations of the analyzed elements, with an average concentration of  $2.65 \mu\text{g}\cdot\text{m}^{-3}$ ), multivariate analyses (enrichment factor and principal components analysis) indicated that most of the elements were not associated with oceanic sources. Over the Southern Ocean, Fe, Cd, As, Al and Cr in the aerosols mainly originated from crustal sources, while Cu, Pb, V and Zn originated from crustal sources and anthropogenic emissions. The enrichment factors ( $EF_{\text{crust}}$ ) for most elements (Fe, Al, As, Cr, Cd, Cu and V) were much lower in the northern latitudes, indicating that when the sampling occurred closer to land the concentrations of these elements in aerosols were strongly affected by terrestrial crustal sources.

**Keywords** aerosol, trace element, multivariate analysis, Southern Ocean, marine

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## 1 Introduction

The atmosphere is a major source of elements such as trace metals like Fe, Cu and Zn, and other elements like N and P, to the open ocean<sup>[1]</sup>. Most trace metals and other elements and compounds are present in the atmosphere as aerosols. Aerosols have atmospheric lifetimes on the order of days to weeks. After long-range transport, large amounts of continental materials, including anthropogenic pollution and its associated trace metals and compounds, are removed from the atmosphere via wet and dry deposition processes over the open ocean<sup>[1]</sup>. The input of metals to the ocean has an important influence on productivity, with metals acting as nutrients and/or toxins<sup>[2]</sup>. Trace metals have also been linked to important atmospheric reactions<sup>[3]</sup>. Previous studies have

found that deposition of atmospheric aerosols into the ocean plays an important role in supplying the nutrients Fe, N and P to the remote ocean<sup>[4]</sup>. However, deposition can also input toxic trace metals into the ocean, which impacts the oceanic biogeochemistry cycle. For example, high deposition of Cu may result in toxicity to microalgae, with implications for the structures of phytoplankton communities<sup>[5-6]</sup>. As such, it is important to study atmospheric trace metals and other elements over oceans.

The Southern Ocean plays a critical role in global climate. With no continental barriers, it serves as a conduit to transmit climatic signals between the Pacific, Atlantic and Indian Oceans<sup>[7]</sup>. The Southern Ocean also plays an important role in the global carbon cycle and climate change<sup>[8]</sup>. Biogeochemical rate processes in the Southern Ocean have an important impact on the global environment<sup>[9]</sup>. Previous studies showed the importance of aerosol iron fertilization over the Southern Ocean, and there is compelling

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evidence that iron supply from a number of sources (such as coastal sediments, aerosols, upwelling, ice melting and enhanced mixing over high topography) influences rates of gross production and carbon export by Southern Ocean ecosystems<sup>[10]</sup>. However, limited field measurements are presently available about the distribution of trace metals and other aerosolized elements in the atmosphere over the Southern Ocean. To better understand the characteristics of atmospheric trace metals and other elements over the Southern Ocean, aerosol samples were collected and analyzed over the Southern Ocean during the 28th cruise of the Chinese National Antarctic Research Expedition (CHINARE). In this study, we present new data on atmospheric elemental concentrations over the Southern Ocean. Atmospheric concentrations of several trace metals and arsenic were analyzed in aerosol samples and we assessed their potential sources using crustal and oceanic indicators.

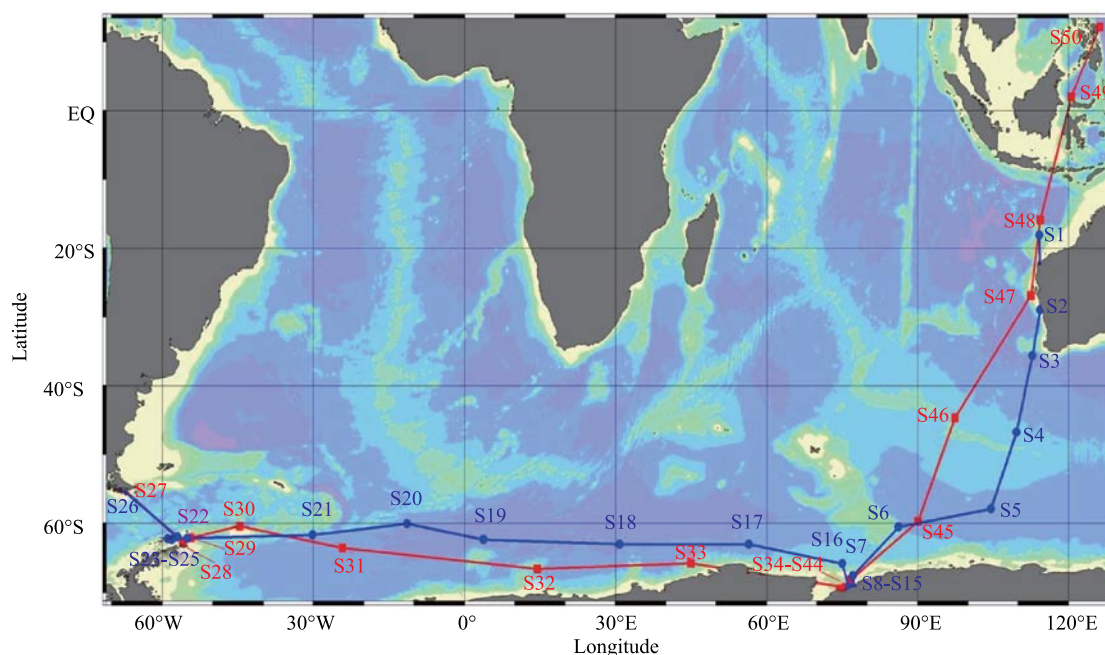
## 2 Materials and methods

### 2.1 Aerosol sample collection

Aerosol samples were collected on the R/V *XUE LONG* icebreaker during the 28th CHINARE. The 28th CHINARE cruise route is presented in Figure 1. The icebreaker set sail from Tianjin, China on 3 November 2011, moved past Fremantle, Australia, landed at the Zhongshan and Great Wall stations in Antarctica and ended its trip in Ushuaia, Argentina. R/V *XUE LONG* icebreaker followed almost the same route on its return and landed in Shanghai on 8 April 2012. The entire trip lasted 163 d and the icebreaker sailed

approximately 28400 nautical miles, approximately 3900 nautical miles of which was ice zone sailing. From Figure 1 it can be seen that aerosol sample collection began when the icebreaker entered the Indian Ocean. The locations where sampling started are marked in Figure 1. Detailed sampling locations and dates are provided in Table 1.

Total suspended particulate matter (TSP) samples were collected using a high volume aerosol sampler (EPL5102) designed and described by Chen et al.<sup>[11]</sup>. The flow rate of the aerosol sampler was set to  $1 \text{ m}^3 \cdot \text{min}^{-1}$ . The aerosol sampler was mounted above the pilot house on the deckhead of the icebreaker, approximately 25 m above the sea surface. A stainless steel shield was installed on the head of the aerosol sampler to protect the samples from being contaminated by the rain, snow or waves. Along with TSP, a station measuring wind direction and speed was installed on the aerosol sampler to avoid anthropogenic pollution and fuel emissions from the ship. Whatman 41 filters were used to collect aerosol samples. Each sample was collected for approximately 48 h. After sampling, the filters were transferred into baked aluminum foil and then ziplock bags, and were stored at  $4^\circ\text{C}$  until analysis. After the study, all of the aerosol samples were transported back to the Key Lab of Global Change and Marine Atmospheric Chemistry of the State Oceanic Administration (GCMAC), Third Institute of Oceanography, State Oceanic Administration for analysis. Other meteorological parameters were collected using an automatic weather station (Vaisala 500). Meteorological parameters were statistically analyzed and are summarized in Table 2. Figure 2 presents the wind direction and wind speed frequencies during the sampling period.



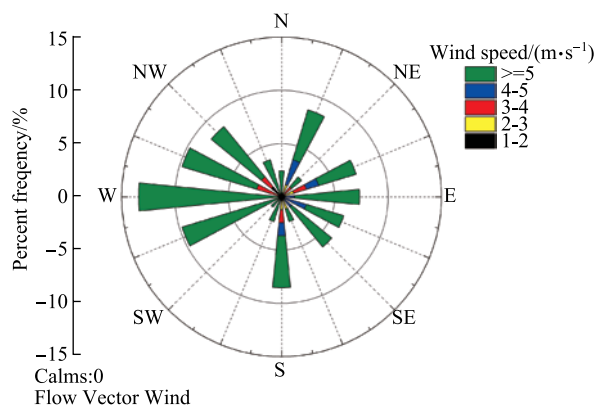
**Figure 1** Route of the 28th CHINARE. The blue line represents the route towards Antarctica and the red line represents the return route from Antarctica. The blue circles and red squares represent the sites where aerosol samples were collected on the way to and from Antarctica, respectively.

**Table 1** Sample dates and locations for aerosol samples collected during the 28th CHINARE

Number	Start date	Start location		End date	End location	
S1	11/14/2011	114.22°E	18.10°S	11/16/2011	114.34°E	28.91°S
S2	11/16/2011	114.36°E	28.97°S	11/20/2011	112.84°E	35.54°S
S3	11/20/2011	112.79°E	35.61°S	11/22/2011	109.64°E	46.76°S
S4	11/22/2011	109.64°E	46.77°S	11/24/2011	104.56°E	57.82°S
S5	11/24/2011	104.53°E	57.87°S	11/26/2011	86.28°E	60.49°S
S6	11/26/2011	86.24°E	60.49°S	11/28/2011	77.09°E	67.50°S
S7	11/28/2011	77.13°E	67.57°S	11/30/2011	77.38°E	69.28°S
S8	11/30/2011	77.37°E	69.28°S	12/2/2011	76.38°E	69.29°S
S9	12/2/2011	76.38°E	69.29°S	12/4/2011	76.38°E	69.29°S
S10	12/4/2011	76.38°E	69.29°S	12/7/2011	76.38°E	69.29°S
S11	12/7/2011	76.38°E	69.29°S	12/9/2011	76.38°E	69.29°S
S12	12/9/2011	76.38°E	69.29°S	12/12/2011	76.38°E	69.29°S
S13	12/12/2011	76.38°E	69.29°S	12/14/2011	76.38°E	69.29°S
S14	12/14/2011	76.38°E	69.29°S	12/16/2011	76.38°E	69.28°S
S15	12/16/2011	76.38°E	69.29°S	12/18/2011	75.21°E	65.95°S
S16	12/18/2011	75.04°E	65.85°S	12/20/2011	56.86°E	62.97°S
S17	12/20/2011	56.49°E	62.98°S	12/22/2011	31.4°E	63.00°S
S18	12/22/2011	30.85°E	63.00°S	12/24/2011	4.43°E	62.49°S
S19	12/24/2011	3.82°E	62.35°S	12/26/2011	11.23°W	60.06°S
S20	12/26/2011	11.37°W	60.06°S	12/28/2011	29.80°W	61.71°S
S21	12/28/2011	30.15°W	61.68°S	12/31/2011	53.26°W	62.01°S
S22	12/31/2011	54.98°W	62.12°S	1/3/2012	58.93°W	62.23°S
S23	1/3/2012	58.93°W	62.23°S	1/5/2012	58.2°W	62.36°S
S24	1/5/2012	58.16°W	62.35°S	1/7/2012	57.16°W	62.07°S
S25	1/8/2012	57.00°W	61.95°S	1/10/2012	68.30°W	54.81°S
S26	1/10/2012	68.30°W	54.81°S	1/13/2012	68.27°W	54.81°S
S27	1/14/2012	67.83°W	54.89°S	1/17/2012	56.02°W	62.79°S
S28	1/17/2012	55.94°W	62.79°S	1/20/2012	54.21°W	62.03°S
S29	1/20/2012	54.41°W	62.06°S	1/24/2012	51.06°W	60.78°S
S30	1/28/2012	44.66°W	60.37°S	1/31/2012	24.50°w	63.52°S
S31	1/31/2012	24.25°W	63.54°S	2/3/2012	14.18°E	66.57°S
S32	2/3/2012	14.44°E	66.57°S	2/5/2012	44.59°E	65.82°S
S33	2/5/2012	44.91°E	65.77°S	2/8/2012	75.93°E	68.99°S
S34	2/10/2012	76.57°E	69.33°S	2/13/2012	76.50°E	69.12°S
S35	2/13/2012	76.38°E	69.22°S	2/15/2012	76.44°E	69.33°S
S36	2/15/2012	76.44°E	69.33°S	2/18/2012	76.16°E	69.27°S
S37	2/18/2012	76.23°E	69.28°S	2/20/2012	76.44°E	69.36°S
S38	2/20/2012	76.45°E	69.36°S	2/23/2012	76.78°E	69.18°S
S39	2/23/2012	75.82°E	69.19°S	2/25/2012	74.41°E	69.47°S
S40	2/25/2012	74.41°E	69.47°S	2/28/2012	74.42°E	69.47°S
S41	2/28/2012	74.42°E	69.47°S	3/2/2012	76.03°E	67.96°S
S42	3/2/2012	76.02°E	69.98°S	3/4/2012	75.30°E	69.41°S
S43	3/4/2012	75.33°E	69.39°S	3/6/2012	76.78°E	68.21°S
S44	3/6/2012	76.78°E	68.17°S	3/8/2012	89.95°E	59.68°S
S45	3/8/2012	90.07°E	59.68°S	3/11/2012	97.40°E	44.64°S
S46	3/11/2012	97.43°E	44.61°S	3/15/2012	115.65°E	31.90°S
S47	3/25/2012	112.54°E	26.91°S	3/27/2012	114.32°E	15.90°S
S48	3/27/2012	114.32°E	15.86°S	3/30/2012	120.46°E	1.92°N
S49	3/30/2012	120.51°E	1.99°N	4/2/2012	126.12°E	12.13°N
S50	4/2/2012	126.12°E	12.15°N	4/5/2012	124.91°E	30.08°N

**Table 2** Meteorological parameters measured during the sampling period

Parameters	Units	Mean±SD	Range
Air pressure	hPa	991.8±12.6	971.7–1026.7
Air temperature	°C	3.3±9.5	-10.7–29.4
R.H.	%	71.5±18.8	42–100
Wind speed	m·s <sup>-1</sup>	9.1±4.3	1–19
Seawater temperature	°C	4.9±8.9	-1.12–29.23

**Figure 2** Wind rose over the whole sampling period.

## 2.2 Elemental analysis

The elemental compositions (Cu, Zn, Cd, Pb, Fe, V, Cr, As, Na and Al) of the aerosol samples were determined using an inductively coupled plasma mass spectrometer (ICP-MS) in a 1000 class clean room at GCMAC. A total metal digest procedure was used to determine the trace metal concentrations in the aerosol samples. Briefly, 1/16 of a filter was cut from each aerosol sample and placed into a clean PTFE digestion tube. Five milliliters of concentrated nitric acid was then added to each sample. After that, the filter was heated and digested using microwave digestion. After digestion, the solution was transferred into a 50-mL PET bottle. The solution was then analyzed using an Agilent 7500ce ICP-MS. Details about the analytical techniques are described in Lin et al.<sup>[12]</sup>. The precision, estimated from the standard deviation of repeat measurements of standards, was less than 5% for the measured elemental compositions; and the recoveries ranged from 96.0% to 108.3%.

## 3 Results and discussion

### 3.1 Mass concentrations of aerosol elements

In this study, seven trace metals (Cu, Zn, Cd, Pb, Fe, V and Cr) and As were quantified. To investigate their sources and distinguish whether they were influenced by crustal or oceanic sources, Al and Na were selected as the crustal and oceanic reference elements, respectively. From Table 1, it

can be seen that 41 aerosol samples (S4–S45) were collected when the icebreaker crossed the Southern Ocean during the 28th CHINARE. Statistical summaries of the 10 aerosol elements over the Southern Ocean are presented in Table 3. We also compared the aerosol elemental concentrations collected in the 28th CHINARE with previous studies<sup>[13–20]</sup> conducted over the Southern Ocean during the 3rd CHINARE, 16th CHINARE, 2010/2011, Antarctic station and other oceanic areas (Table 4).

**Table 3** Statistical summaries of elemental concentrations in aerosol samples collected over the Southern Ocean during the 28th CHINARE

Elements	N	Mass concentrations/(ng·m <sup>-3</sup> )				
		Minimum	Median	Maximum	Mean	SD
Cu	41	0.242	0.808	3.034	0.957	0.638
Zn	41	0.505	1.928	8.984	2.584	1.930
Cd	41	0.004	0.010	0.178	0.017	0.029
Pb	41	0.025	0.094	0.519	0.127	0.098
Fe	41	4.561	13.059	420.285	28.824	64.967
V	41	0.047	2.552	39.531	5.541	7.534
Cr	41	0.129	0.255	0.660	0.298	0.145
As	41	0.004	0.014	0.132	0.020	0.021
Na	41	167.714	2032.360	8817.671	2655.252	2176.468
Al	41	1.747	6.945	206.050	12.559	31.514

Over the Southern Ocean, the average concentration of Na in aerosol samples was  $2.65 \pm 2.18 \mu\text{g}\cdot\text{m}^{-3}$ , ranging from 0.17 to  $8.82 \mu\text{g}\cdot\text{m}^{-3}$ , more than one or two orders of magnitude greater than the other elements measured. Similarly high concentrations of Na have also been measured at the Zhongshan Station<sup>[15–16]</sup> (Table 4). Na represents sea salt aerosols over the ocean<sup>[13,17]</sup>. The higher Na concentrations over the Southern Ocean indicated that there is a tremendous amount of sea salt in the marine atmosphere. This implies that sea spray is a significant aerosol source over the Southern Ocean. Previous studies of water soluble inorganic ions in aerosols over the Southern Ocean and Antarctica also found that sea salt particles contributed substantially to the total marine aerosol mass relative to other aerosol species<sup>[21–23]</sup>. The concentrations of Al ranged from 1.747 to  $206.050 \text{ ng}\cdot\text{m}^{-3}$ , with an average of  $12.599 \pm 31.514 \text{ ng}\cdot\text{m}^{-3}$ . In comparison with previously reported Al concentrations in Table 4, the Al concentrations in this study were lower than those during the 16th CHINARE, over the Zhongshan Station and the western Indian Ocean, except over the mid-Indian Ocean. The lower concentrations suggested that crustal matter source contributions were much lower than marine aerosol source contributions over the Southern Ocean.

Fe was the most abundant trace metal in the aerosols collected over the Southern Ocean. Fe concentrations varied from 4.561 to  $420.285 \text{ ng}\cdot\text{m}^{-3}$ , with an average of  $28.824 \pm 64.967 \text{ ng}\cdot\text{m}^{-3}$ . These concentrations were slightly

higher than those previously reported everywhere in the study area except the eastern Indian Ocean (Table 4). Fe is an important nutrient limit element that can enhance primary productivity in some oceanic areas<sup>[24]</sup>. Higher concentrations of Fe in the Southern Ocean atmosphere may be an important potential factor, which can positively influence Southern Ocean ecosystems. Relatively high concentrations of V were measured. The average concentration of V was  $5.541 \pm 7.534 \text{ ng}\cdot\text{m}^{-3}$ , ranging from 0.047 to  $39.531 \text{ ng}\cdot\text{m}^{-3}$ . From Table 4, it can be seen that the average V concentrations over the Southern Ocean were much higher than that over the Antarctic stations<sup>[25]</sup>, Antarctic Ocean and those studied during the 16th CHINARE, except in the western Pacific. V is generally identified as a marker of oil combustion<sup>[26]</sup>. Zn concentrations ranged from 0.505 to  $8.984 \text{ ng}\cdot\text{m}^{-3}$ , with an average of  $2.584 \pm 1.930 \text{ ng}\cdot\text{m}^{-3}$ . Although the concentrations

of Zn were higher than those for other elements (Pb, Cd, Cr and As), the concentrations measured in this study were much lower than previous results from the 16th CHINARE, Zhongshan Station and Antarctic Ocean. The average concentration of Cu in aerosol samples over the Southern Ocean was  $0.957 \pm 0.638 \text{ ng}\cdot\text{m}^{-3}$ , ranging from 0.242 to  $3.034 \text{ ng}\cdot\text{m}^{-3}$ . Pb concentrations in the Southern Ocean atmosphere ranged from 0.025 to  $0.519 \text{ ng}\cdot\text{m}^{-3}$ , with an average of  $0.127 \pm 0.098 \text{ ng}\cdot\text{m}^{-3}$ . These concentrations were lower than in other locations in the area, except Prydz Bay. Cd and As concentrations in the aerosols were markedly lower than other elemental concentrations in the Southern Ocean. The average concentrations of Cd and As were  $0.017 \pm 0.029 \text{ ng}\cdot\text{m}^{-3}$  and  $0.020 \pm 0.021 \text{ ng}\cdot\text{m}^{-3}$ , respectively. The concentrations of these two elements were generally in agreement with those reported previously.

**Table 4** Comparison with data from previous studies

Site	Sampling period	Mass concentrations/( $\text{ng}\cdot\text{m}^{-3}$ )										References
		Cu	Zn	Cd	Pb	Fe	V	Cr	As	Na	Al	
Southern Ocean	2011.11–2012.4 28th CHINARE	0.957	2.584	0.017	0.127	28.824	5.541	0.298	0.02	2655.252	12.559	This study.
North Pacific		2.7	–	0.05	1.9	16.4	–	–	–	–	–	
South Pacific		0.01	–	0.0002	0.62	0.32	–	–	–	–	–	
Antarctic Ocean	1986.11–1987.5	2.3	–	0.02	1.1	4.6	–	–	–	–	–	
South Atlantic Ocean	3rd CHINARE	1.3	–	0.09	11.5	3.1	–	–	–	–	–	[13]
North Indian Ocean		0.4	–	0.02	2	9.6	–	–	–	–	–	
Near shore		4.3	–	0.68	15	39.6	–	–	–	–	–	
Southern Ocean		0.70	12.91	0.04	0.23	21.95	2.13	0.61	–	–	69.41	
Western Pacific	1999.11–2000.4	5.27	75.1	0.4	5.69	236	12.54	4.64	–	–	496.1	
East Indian Ocean	16th CHINARE	1.22	4.74	0.07	1.03	45.23	1.75	0.69	–	–	110	[14]
Prydz Bay		0.46	14.62	0.03	0.08	5.06	1.26	0.37	–	–	43.19	
Zhongshan Station	1998.3–1999.2	1.28	8.353	0.07	0.559	19.75	0.578	0.768	–	2124	38.87	[15]
Zhongshan Station	1998.3–1999.11	0.778	6.655	0.047	0.431	14.92	0.64	0.626	–	1928	32.91	[16]
Southern Ocean Coastal		–	–	0.004	–	14	–	–	–	1100	150	
East Antarctica	2010.11–2011.3	–	–	0.017	–	26	–	–	–	990	190	[17]
Antarctic Ocean												
60°–69°S, 14°–8°W	1990	0.17	7.58	0.10	0.27	–	0.04	0.33	0.02	–	–	[18]
Western Indian Ocean	2007	1.80	8.70	0.01	0.56	12.29	–	–	–	–	33.99	[19]
Mid-Indian Ocean	2002	1.84	1.44	0.002	0.15	7.26	–	0.68	–	–	4.59	[20]

## 3.2 Source apportionment

### 3.2.1 Enrichment factors

Major sources of the elements quantified were investigated using a series of statistical analyses. Correlation coefficients between elements were calculated and are shown in Table 5. Significant positive correlation coefficients were found between Fe and Al ( $r=0.944$ ,  $p=0.01$ ), As and Al ( $r=0.861$ ,  $p=0.01$ ), and Pb and Al ( $r=0.627$ ,  $p=0.01$ ), which suggested

that Fe, As and Pb may have the same source(s) as Al. Al is usually considered as an indicator element for crustal matter<sup>[27]</sup>, so this suggests that the primary source of Fe, As and Pb may be crustal matter. Cr also correlated well with Al ( $r=0.307$ ,  $p=0.05$ ), suggesting a crustal source. Significant positive correlation coefficients between Pb and Fe with Cr and As indicated that these elements has similar sources. Zn also correlated well with Pb and As. Cu had a negative correlation with Na ( $r=-0.484$ ,  $p=0.01$ ), while Cd had no significant correlation with the other elements.

**Table 5** Relationships between elemental concentrations

	Cu	Zn	Cd	Pb	Fe	V	Cr	As	Na	Al
Cu	1	-0.025	-0.182	-0.006	0.066	-0.001	0.164	-0.043	-0.484**	0.019
Zn		1	-0.122	0.410**	0.300	0.186	0.169	0.379*	0.003	0.228
Cd			1	-0.084	-0.016	-0.138	-0.144	-0.019	0.047	0.020
Pb				1	0.750**	0.103	0.406**	0.704**	-0.064	0.627**
Fe					1	-0.058	0.411**	0.893**	-0.056	0.944**
V						1	-0.071	0.213	0.110	-0.069
Cr							1	0.338*	0.028	0.307*
As								1	0.056	0.861**
Na									1	0.007
Al										1

Note: \*\* represents  $p=0.01$ , while \* represents  $p=0.05$ .

Enrichment factors ( $EF$ ) were also calculated to investigate the elements' sources.  $EF$ s are widely used to assess whether the elements in aerosols are influenced by crustal, oceanic or anthropogenic sources<sup>[13-14,17,20,28]</sup>. In this work, Al was used as an indicator element for crustal enrichment calculations, while Na was used as an indicator for sea salt enrichment calculations. The  $EF$  formulas are shown in Equations 1 and 2:

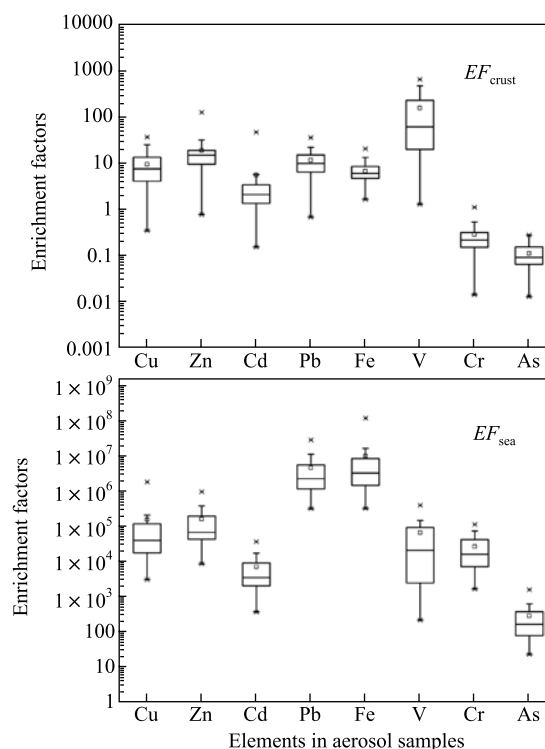
$$EF_{i,crust} = \frac{(C_i/C_{Al})_{aerosol}}{(C_i/C_{Al})_{crust}} \quad (1)$$

$$EF_{i,sea} = \frac{(C_i/C_{Na})_{aerosol}}{(C_i/C_{Na})_{sea}} \quad (2)$$

where  $EF_{i,crust}$  is the  $EF_{crust}$  value for element  $i$ ,  $EF_{i,sea}$  is the  $EF_{sea}$  value for element  $i$ ;  $(C_i/C_{Al})_{aerosol}$  is the ratio derived from the concentrations of element  $i$  and Al in aerosol samples, and  $(C_i/C_{Al})_{crust}$  is the ratio derived from the concentrations of element  $i$  and Al in crustal materials<sup>[29]</sup>;  $(C_i/C_{Na})_{aerosol}$  is the ratio derived from the concentrations of element  $i$  and Na in aerosol samples, while  $(C_i/C_{Na})_{sea}$  is the ratio derived from the concentrations of element  $i$  and Na in seawater<sup>[30]</sup>. Previous studies<sup>[17,20,28]</sup> have reported that if the  $EF_{i,crust}$  value is below 10, then element  $i$  can be considered as a crustal source, while if the value  $>10$  the element could be from other sources like anthropogenic pollution.  $EF_{i,sea}$  values  $<10$  were taken to be indicative of a marine source, while  $EF_{i,sea}$  values  $>10$  suggested another source. The presence of high  $EF$  values with respect to both crustal and seawater composition suggests that anthropogenic processes may be important<sup>[20]</sup>.

Figure 3 presents box-and-whisker plots of crustal and sea salt enrichment factors. Although As is usually considered to be a good tracer for coal emissions, it can be seen that As had the lowest  $EF_{crust}$  values (lower than 1) in the remote Southern Ocean and As correlated well with Al, which indicated that this element likely originated from crustal sources. Cr also had low  $EF_{crust}$  values (most  $EF$ s were lower than 1), suggesting a crustal source. Although no

significant correlation was observed between Cd and Al, the  $EF_{crust}$  values for Cd were mainly lower than 10, suggesting it may also originate from a crustal source. The  $EF_{crust}$  values for Cu and Pb ranged between 1 and 100, with the median values being approximately 10, suggesting that Cu and Pb potentially originated from crustal and anthropogenic sources. The crustal enrichment factors for Zn also ranged from 1 to 100, but most of the values were higher than 10, suggesting that Zn mainly originated from anthropogenic sources. Fe has diverse sources to the atmosphere; it is associated with crustal dust and, to a lesser extent, anthropogenic sources<sup>[24]</sup>. In this study, the  $EF_{crust}$  values for Fe were mainly lower than 10 and Fe correlated well with Al, indicating that most of the Fe originated from crustal sources with little anthropogenic input. V had the highest  $EF_{crust}$  values. V is a good tracer for oil combustion<sup>[26]</sup>, so the high  $EF_{crust}$  values for V suggested that the primary source of this trace metal in the remote Southern Ocean was anthropogenic pollution. As shown in Figure 3, Cu, Zn, Cd, Pb, Fe, V, Cr and As all had  $EF_{sea}$  values higher than 10, suggesting that these elements did not originate from the ocean.



**Figure 3** Box-and-whisker plots of crustal and sea salt enrichment factors for the elements in aerosol samples collected over the Southern Ocean during the 28th CHINARE.

### 3.2.2 Principal components analysis

Principal components analysis (PCA) was used to analyze the elemental concentrations. PCA is a statistical tool in multivariate data analysis to reduce the number of dimensions in a dataset<sup>[31]</sup>. It uses an orthogonal linear transformation that converts the data to a new coordinate

system such that the greatest variance by some projection of the data comes to lie on the first principal component (or the first coordinate), the second greatest variance on the second coordinate, and so on<sup>[32]</sup>. Previous studies have used this method combined with reference elements to assess aerosol sources<sup>[14,28]</sup>. The PCA analysis results are presented in Table 6. The components were rotated using the varimax method.

**Table 6** Rotated component matrix of elements from aerosols collected over the Southern Ocean

	Component		
	$F_1$	$F_2$	$F_3$
Cu	0.024	<b>-0.854</b>	0.084
Zn	0.394	0.065	<b>0.528</b>
Cd	0.010	<b>0.321</b>	<b>-0.612</b>
Pb	<b>0.823</b>	-0.015	0.197
Fe	<b>0.974</b>	-0.042	-0.057
V	-0.029	0.186	<b>0.766</b>
Cr	<b>0.499</b>	-0.213	0.085
As	<b>0.917</b>	0.129	0.161
Na	-0.023	<b>0.797</b>	0.102
Al	<b>0.923</b>	0.032	-0.123
Eigenvalues	3.781	1.570	1.295
% of variance	37.81	15.70	12.95
Cumulative/%	37.81	53.52	66.46

Note:  $F_1$  is the first principal component or the first factor;  $F_2$  is the second principal component or the second factor;  $F_3$  is the third principal component or the third factor.

Three principal components were extracted with eigenvalues greater than 1.0. They accounted for approximately 66.46% of the total variance. The first principal component,  $F_1$ , accounted for 37.81% of the variance. Al, Fe, As and Pb had high loadings in  $F_1$ , suggesting that these elements were strongly influenced by crustal sources. Cr had moderate loadings in  $F_1$ , indicating that it may also be affected by crustal sources. The second principal component ( $F_2$ , 15.70% of the variance) showed high loadings of Na and Cu. The negative value for Cu indicated it had a negative correlation with sea salt. Cd had low loading in  $F_2$ , suggesting that some Cd may be emitted by the ocean. The third principal component ( $F_3$ , 12.95% of the variance) had high loadings for V. Because V typically originates from oil combustion,  $F_3$  represents anthropogenic pollution. Zn also had moderate loadings in  $F_3$ . Zn is released from the combustion of fossil fuels, industrial metallurgical processes and waste incineration<sup>[33]</sup>. Thus, Zn in the aerosols over the Southern Ocean may originate from the transport of anthropogenic pollution. Overall, elemental concentrations of aerosols in the Southern Ocean were mainly affected by crustal, oceanic and anthropogenic sources. These results were slightly different to a previous study in the Southern Ocean by Huang et al.<sup>[14]</sup> During the 16th CHINARE, the elemental concentrations were mainly influenced by the same sources we have identified.

### 3.3 Spatial distributions

#### 3.3.1 Spatial variations in mass concentrations

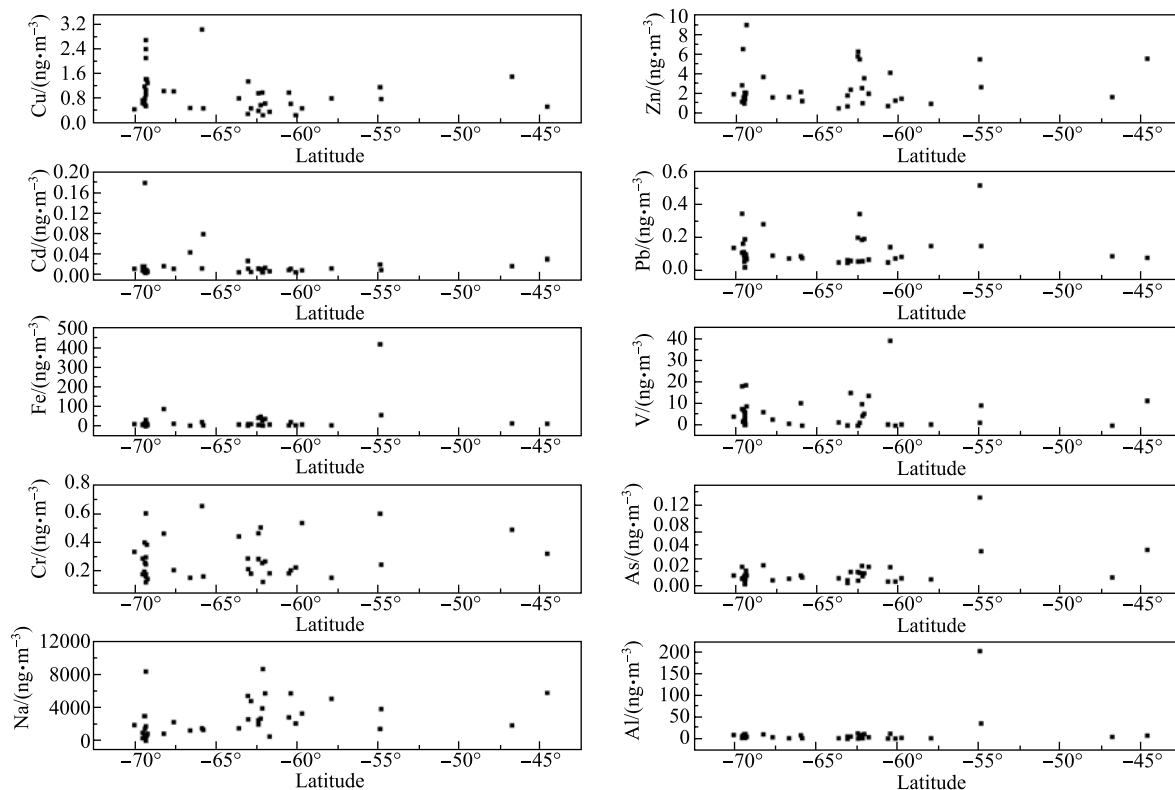
To further investigate the aerosol sources and long-range transport of aerosols to the Southern Ocean, spatial variations in elemental mass concentrations over the Southern Ocean and enrichment factors throughout the entire route were studied. The latitudinal mass concentration distributions of selected elements are presented in Figure 4. Most of the samples were collected to the south of  $\sim 60^\circ\text{S}$ . Mass concentrations of Fe, As and Al were lower between  $45^\circ\text{S}$  and  $70^\circ\text{S}$ , except for the peak values at  $55^\circ\text{S}$ . Pb also had the highest concentrations at this location. Combined with the sampling information in Table 1, the highest Fe, As, Al and Pb concentrations were measured near Ushuaia (latitude  $54.8^\circ\text{S}$ ), Argentina, on 10–13 January 2012. Air mass back trajectory analyses indicated that highest concentrations of these crustal elements were associated with air masses from South America (Figure 5a). After removing the highest concentrations, the average concentrations of Fe, As and Al were 19.038, 0.018 and  $7.722 \text{ ng}\cdot\text{m}^{-3}$ , respectively. These average concentrations represented the background concentrations over the Southern Ocean. From Table 4, it can be seen that the average concentrations of these three elements were comparable with those from previous studies over the Southern Ocean<sup>[13,17]</sup>. The concentrations of Fe measured in this study were similar to the total Fe concentrations measured in the Southern Ocean by Gao et al.<sup>[34]</sup>. Low Cu concentrations were measured from  $45^\circ\text{S}$  to  $65^\circ\text{S}$ , while higher Cu concentrations were measured at  $69^\circ\text{S}$  over coastal Antarctica. Although the latitudinal distributions of Cr were different from those of Cu, the highest concentrations of Cu and Cr were found near  $66^\circ\text{S}$ . One explanation for the highest concentrations of Cu and Cr could be possible contributions from local Antarctic sources based on air mass trajectory analysis (Figure 5b). Most mass concentrations of Zn were lower than  $4 \text{ ng}\cdot\text{m}^{-3}$ , with several higher concentrations measured at  $63^\circ\text{S}$  and  $69^\circ\text{S}$ ; the highest concentration of Zn was measured at  $69^\circ\text{S}$  over coastal Antarctica. Mass concentrations of Cd were very low ( $<0.10 \text{ ng}\cdot\text{m}^{-3}$ ) over the Southern Ocean, except for the highest value measured near  $69^\circ\text{S}$  over coastal Antarctica. The air mass trajectory associated with highest concentrations of Zn and Cd suggested that there may be sources of these two elements around coastal Antarctica (Figures 5c, 5d). This result was similar to that reported by Xu et al.<sup>[17]</sup>, where higher average concentrations of Cd over coastal east Antarctica were measured than those over the Southern Ocean during the austral summer of 2010/2011. V and Zn had similar latitudinal distributions, although the highest concentrations of V were measured near  $60^\circ\text{S}$  and two other high concentrations of V were measured near  $69^\circ\text{S}$  in coastal Antarctica. Air mass back trajectories associated with the three highest and lowest concentrations of V are shown in Figures 5e–5h. High V concentrations were associated with air masses from coastal Antarctica, while clean air masses

from across the ocean carried the lowest concentrations of V. Anthropogenic activities like oil combustion, shipping and helicopter traffic around coastal Antarctic research stations could be responsible for anthropogenic emissions of V<sup>[23]</sup>. The highest Na concentrations were measured between 60°S and 63°S, and its concentrations may have been affected by strong westerly winds. Sea spray or bubble bursting processes were the dominant source of sea salt in this area<sup>[17]</sup>. Budhavant et al.<sup>[23]</sup> also found contributions of marine elements (Na, Cl and Mg) were higher over the Southern Ocean and that the main source of sea salt production over the open ocean was sea spray droplets.

### 3.3.2 Spatial variations of enrichment factors

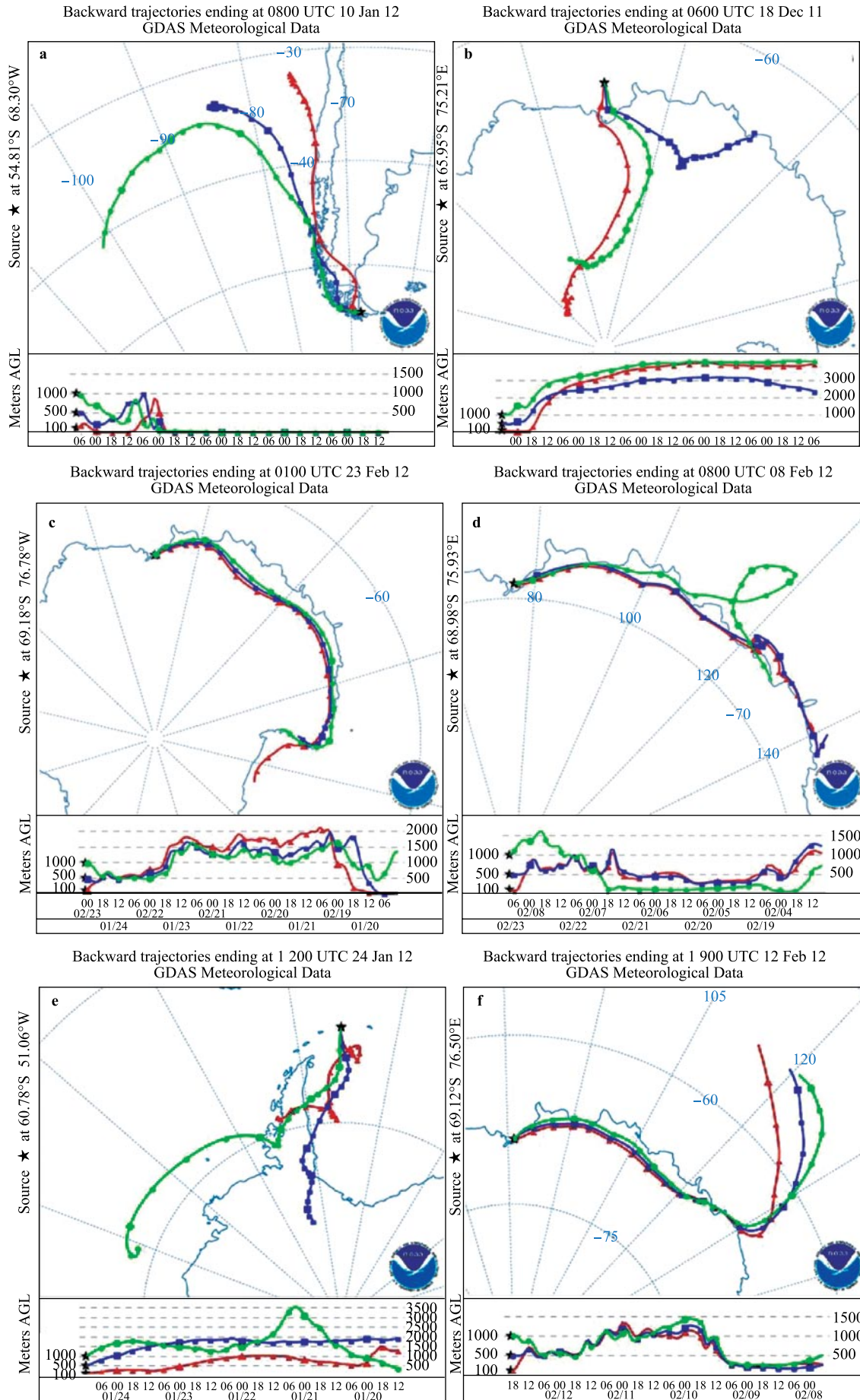
Because the  $EF_{sea}$  of all the selected elements were higher than 10, we only considered spatial variations of the  $EF_{crust}$  to study the impacts of terrestrial crustal matter and anthropogenic activities on the Southern Ocean. Latitudinal distributions of  $EF_{crust}$  during the entire route are shown in Figure 6. Between 30°S and 20°N, Cu mainly originated from crustal sources, with  $EF_{crust}$  values lower than 10. Values around 10 over the Southern Ocean indicated that besides long-range crustal matter transport, anthropogenic activities may also play a role in Cu concentrations.  $EF_{crust}$  values for Cr and As were lower than 10 during the entire route, indicating that these two elements were mainly from crustal sources. Spatial distributions of  $EF_{crust}$  for Fe were similar to those for As and Cr, and the majority of the  $EF_{crust}$  values for Fe were lower than 10. The Fe enrichment factor values

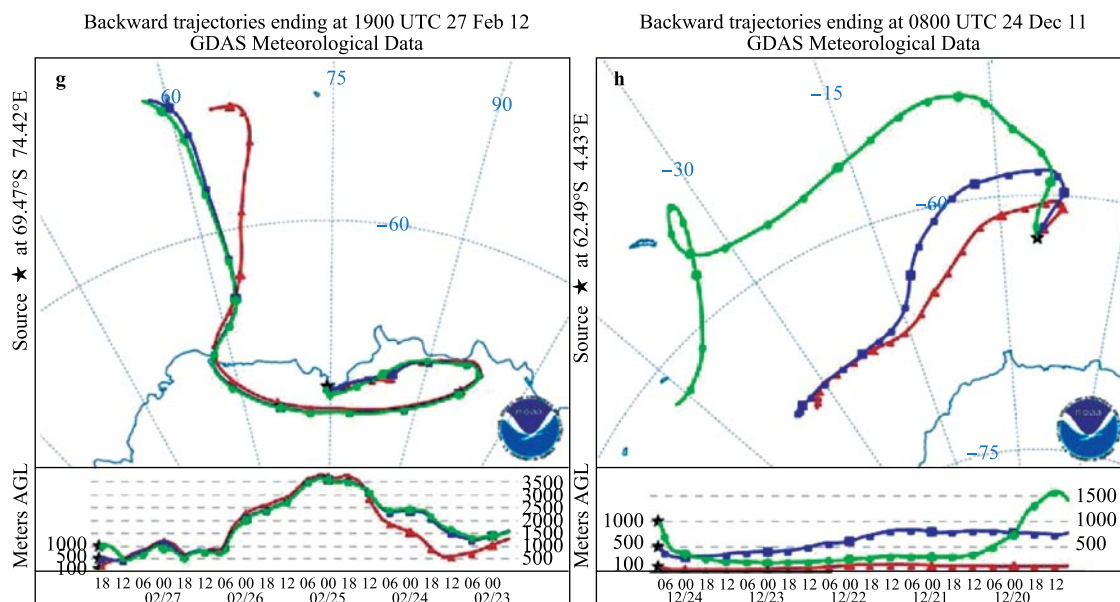
showed a decreasing trend with latitude from south to north. A few  $EF_{crust}$  values for Fe were greater than 10 near 69°S over coastal Antarctica. These values may be associated with air masses from coastal Antarctica according to Gao et al.<sup>[34]</sup>. Higher Fe concentrations were also observed in coastal east Antarctica. From Figure 6, it is apparent that  $EF_{crust}$  values for V also decreased from southern latitudes to northern latitudes. Except at 35°S, the  $EF_{crust}$  values for V from 50°S to 20°N were lower than 10, indicating a terrestrial crustal matter source of V in this area. The high value at 35°S was measured near Fremantle, Australia, and it may have been affected by exhaust emissions from the port. Many high  $EF_{crust}$  values for V (>10) were measured between 55°S and 70°S near the Antarctic. From Figure 5, it can be seen that high concentrations of V were associated with air masses from the Antarctic. V was a good marker for oil combustion and it likely originated from anthropogenic pollution. Low concentrations and  $EF_{crust}$  values of V during the entire route proved that the wind direction and wind speed control system installed on the aerosol sampler can effectively prevent fuel exhaust emissions from the R/V *XUE LONG* icebreaker being measured. However, during austral summer, scientific expeditions over the Southern Ocean and Antarctic increased and shipping activities, movements of helicopters and other human activities like oil combustion at Antarctic research stations could be responsible for anthropogenic emissions of V<sup>[23]</sup>. Harbors in South America and Australia may be another potential source of V over the Southern Ocean. Strong westerly winds may carry the elements into the Southern Ocean. Most of the  $EF_{crust}$  values for Pb over the Southern



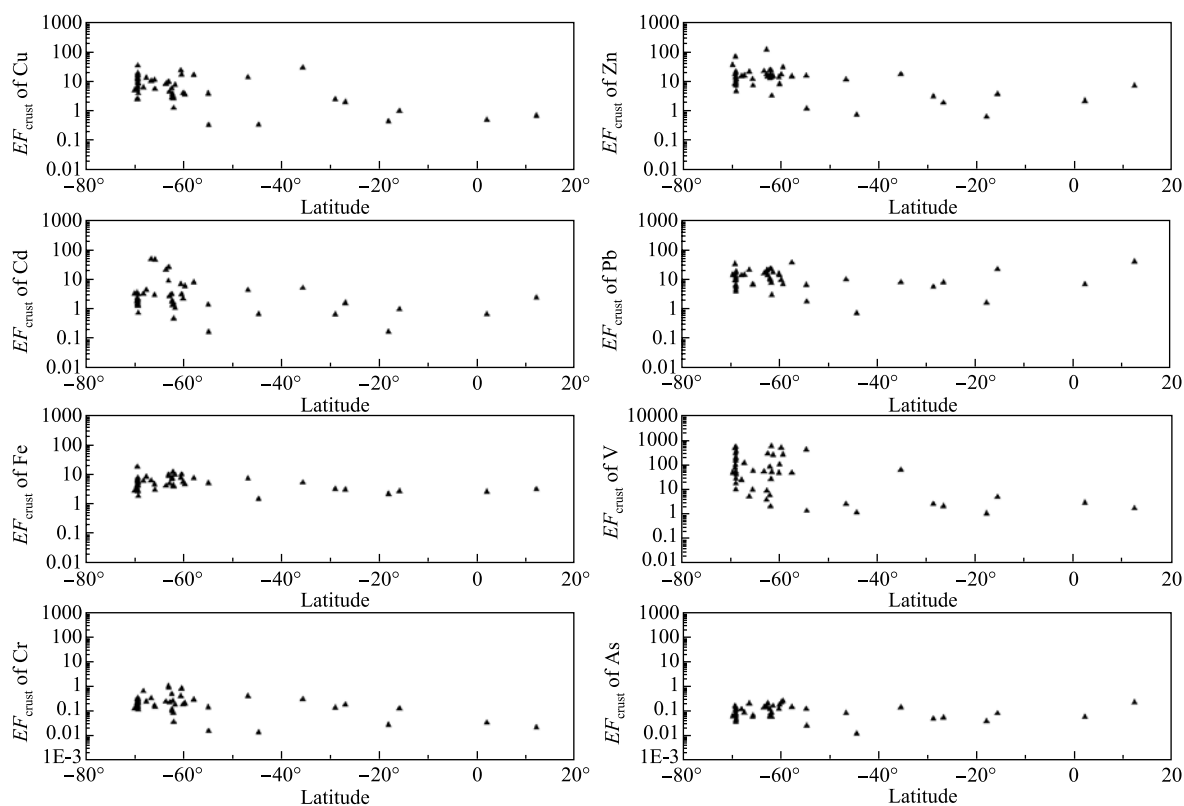
**Figure 4** Latitudinal mass concentration distributions of selected elements over the Southern Ocean.







**Figure 5** Air mass back trajectories ending at the sampling sites over the Southern Ocean. Air mass back trajectories associated with **a**, the highest concentrations of Pb ( $0.519 \text{ ng}\cdot\text{m}^{-3}$ ), Fe ( $420.285 \text{ ng}\cdot\text{m}^{-3}$ ), As ( $0.132 \text{ ng}\cdot\text{m}^{-3}$ ) and Al ( $206.050 \text{ ng}\cdot\text{m}^{-3}$ ); **b**, the highest concentrations of Cu ( $3.034 \text{ ng}\cdot\text{m}^{-3}$ ) and Cr ( $0.66 \text{ ng}\cdot\text{m}^{-3}$ ); **c**, the highest concentration of Zn ( $8.984 \text{ ng}\cdot\text{m}^{-3}$ ); **d**, the highest concentration of Cd ( $0.178 \text{ ng}\cdot\text{m}^{-3}$ ); **e**, the highest concentration of V ( $39.531 \text{ ng}\cdot\text{m}^{-3}$ ); **f**, the second highest concentration of V ( $18.787 \text{ ng}\cdot\text{m}^{-3}$ ); **g**, the third highest concentration of V ( $18.53 \text{ ng}\cdot\text{m}^{-3}$ ); **h**, the lowest concentration of V ( $0.047 \text{ ng}\cdot\text{m}^{-3}$ ).



**Figure 6** Latitudinal distributions of  $EF_{\text{crust}}$  during the entire route.

Ocean were lower than 10, suggesting that the major sources of Pb were crustal sources. Some scattered  $EF_{\text{crust}}$  values for Pb over the Southern Ocean may be associated with

the human activities in Antarctica or long-range transport from the continents. North of  $40^\circ\text{S}$ ,  $EF_{\text{crust}}$  values for Pb gradually increased and most of the values were greater

than 10, indicating that Pb originated from anthropogenic pollution.  $EF_{\text{crust}}$  values for Zn were similar to those for V, suggesting that crustal matter was the major source north of 30°S, while anthropogenic pollution could be another source over the Southern Ocean. Most of the  $EF_{\text{crust}}$  values for Cd were lower than 10, suggesting that the major source of Cd along the entire route was crustal matter. A few values higher than 10 over the Southern Ocean could have originated from other sources, such as biogenic emissions and volcanic eruptions<sup>[17]</sup>. Overall, the enrichment factors ( $EF_{\text{crust}}$ ) for most elements were much lower at northern latitudes, indicating that when the sampling sites were closer to the continents the elemental concentrations were strongly affected by terrestrial crustal matter sources.

## 4 Conclusions

Aerosol samples were collected over the Southern Ocean during the 28th CHINARE. To study the elemental composition characteristics, trace metals (Cu, Zn, Cd, Pb, Fe, V, and Cr), As, Na and Al in the marine aerosol samples were analyzed using ICP-MS. Fe was the most abundant trace metal. V and Zn also had high concentrations. Na concentrations were the highest overall and indicated that sea spray is a significant aerosol source over the Southern Ocean. The  $EF_{\text{crust}}$  values for the elements suggested that Cr, As, Cd and Fe were mainly influenced by the crustal sources. Cu, Pb, V and Zn were affected by crustal and anthropogenic sources. The  $EF_{\text{sea}}$  values suggested that the trace metals (Cu, Zn, Cd, Pb, Fe, V and Cr) and As had little correlation with sea spray. The elements were also classified into three main groups using PCA. Pb, Fe, Cd, As and Al (the first principal component) in the aerosols were strongly affected by crustal sources, which accounted for 37.81% of the variance. Na was in the second group, which was oceanic sources; while V and Zn were mainly affected by anthropogenic emissions from Antarctica and long-range transport from the continents. The latitudinal mass concentration distributions of crustal elements were similar over the Southern Ocean and high concentrations of these elements mainly originated from South America. While other elements showed different spatial distributions, high values of V, Cu, Cr and Zn were associated with air masses from Antarctica. Spatial distributions of  $EF_{\text{crust}}$  showed that Fe, Cr, As and Cd mainly originated from crustal matter over the Southern Ocean, while Cu, Pb, V and Zn were not only from crustal sources, but were also affected by anthropogenic activities.  $EF_{\text{crust}}$  values for most elements were much lower at northern latitudes, suggesting that when the sampling sites were closer to the continents more elements originated from terrestrial crustal matter sources.

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