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Earth and Planetary Science Letters 234 (2005) 249–259

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Trace elements in Vostok Antarctic ice during the last four climatic cycles

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Received 29 September 2004; received in revised form 24 February 2005; accepted 9 March 2005
Available online 21 April 2005
Editor: E. Bard

Abstract

Li, V, Cr, Mn, Co, As, Rb, Sr, Ba, Bi and U were determined by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) in various sections of the 3623 m Vostok deep Antarctic ice core dated from 4600 to 410,000 years BP, which corresponds to the last four climatic cycles back to isotopic stage 11.3. Concentrations of all elements were found to be highly variable with low values during interglacial periods and warm interstadials and much higher values during the coldest periods of the last four ice ages. Crustal enrichment factors suggest various sources for the different elements. Rock and soil dust is the dominant source of V, Mn, Rb, Ba and U whatever the period, and of Li, Cr, Co, Sr and As during cold periods. Sea salt aerosol, together with aeolian dust, also contributes significantly to Sr whereas volcanic emissions could provide a significant input for As and Bi especially during warm periods.

Keywords: Vostok; trace elements; ice; climate

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doi:10.1016/j.epsl.2005.03.001

1. Introduction

Deep Antarctic ice cores have the potential to give unique information on past natural changes in the biogeochemical cycles of trace elements. Deciphering these frozen archives for trace elements has however proved to be exceedingly difficult because of the very high purity of Antarctic snow and ice, which makes it a challenge to obtain fully reliable data from the analysis of ice cores whose outside is heavily contaminated during drilling operations. The impetus in the field came from the pioneering work of Clair Patterson and his colleagues at the California Institute of Technology. They developed the first ultra-clean procedures to efficiently decontaminate deep polar ice cores by mechanically chiseling off successive veneers of ice in progression from the contaminated outside to the center, in order to obtain the uncontaminated inner part of the core [1].

Until now these methods were only used to analyze ice cores of intermediate depths (less than 1 km), because such cores can be obtained from drill holes not requiring a wall retaining fluid, which greatly reduces the contamination of the outside of the core [2]. The main drawback of this is that these cores only cover rather short time periods (~40,000 years, for the 905 m core drilled at Dome C in 1978, for instance [3]).

As such these methods were never used for the comprehensive analysis of very deep Antarctic ice cores that cover several climatic cycles, such as the 3623 m Vostok core [4] or the newly drilled 3190 m EPICA Dome C core [5]. The huge pressure encountered at these depths makes it mandatory to fill the drilling hole with a wall retaining fluid, which results in an enormous contamination of the outside of the core sections. The few attempts which were made to analyze such very deep cores for heavy metals were largely unsuccessful: even the most central parts of the cores were found to be contaminated, probably because a significant fraction of the external contamination was transferred towards the center during the decontamination of the sections [6–8].

The extremely time consuming analytical efforts needed are recompensed by the fact that trace element studies in deep ice cores provide remarkable information about the changes in different biogeochemical cycles over the last climatic cycles. Heavy metals can in fact help us to distinguish between the different natural sources from which the particles and the aerosol transported over Polar Regions have originated. Rock and soil dust, marine aerosol and volcanic emissions were the three main contributors to the overall heavy metals input in Polar Regions during the pre-industrialized period. They constituted important components that interact with atmospheric processes that could produce positive and/or negative feedback mechanisms influencing climate. As an example, the considerable glacial dust input to East Antarctica can be explained by the synergy of several factors involving the atmosphere, the ocean, the biosphere and the lithosphere. In this context a key role is played by the increased aridity of the continents due to changes in soil moisture and/or vegetation cover, as well as the enlargement of the dust-source areas caused by a drop in sea-level. In addition, the reduction in the intensity of the hydrological cycle leads to less efficient scavenging by precipitation and consequently a more efficient transport of dust.

We present here comprehensive data on past changes in the occurrence of various trace elements (Li, V, Cr, Mn, Co, As, Rb, Sr, Ba, Bi and U) in Antarctic ice during the last four climatic cycles (the past ~410,000 years). They were obtained by analyzing various sections of the upper 3285 m of the 3623 m Vostok ice core, using improved decontamination procedures and highly sensitive inductively coupled plasma sector field mass spectrometry (ICP-SFMS).

2. Experimental procedures

2.1. Core sections

The 3623 m Vostok ice core was drilled from a fluid (kerosene) filled hole at the Russian Vostok Station (78°28′S, 106°48′E, elevation 3488 m, mean annual temperature −55 °C) in East Antarctica. Thirty-seven sections (length 35–45 cm, diameter 10 cm) were selected from the part of the core, which corresponds to the last four climatic cycles (the last ~410,000 years). The detailed deuterium profile previously published by Petit et al. [9], Fig. 1, allowed us to select sections dated from the successive climatic stages [10]. Parts of the sections were chosen from the Holocene, the last interglacial period (Marine

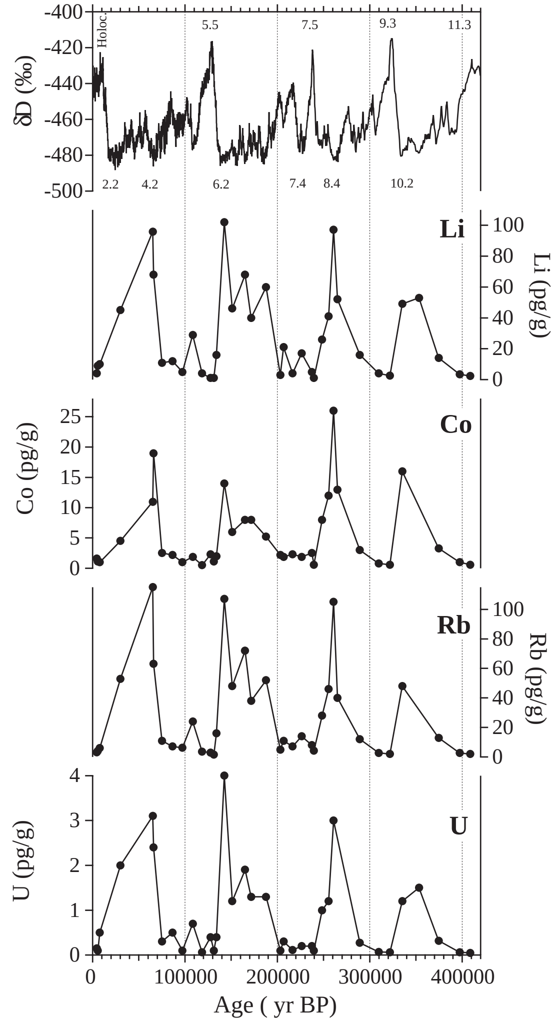

Fig. 1. Vostok Antarctic ice core: changes in Li, Co, Rb and U concentrations as a function of the age of the ice during the last four climatic cycles (the past ~410,000 years). Also shown at the top of the figure is the deuterium profile from Petit et al. [9], with Marine Isotope Stage (MIS) numbers from Bassinot et al. [10]. D, expressed in per mil δ units (δD), is used as a proxy of temperature, with less negative values indicating higher temperatures during interglacial periods and more negative values showing cold climatic stages. The uncertainty of the measurements for all samples was extrapolated from the results of in depth studies for only a few samples, because of the very low sample volumes available for most of the samples. The overall precision of the data was found to range from 2% for Sr to 15% for As (see Sec. 2.4).

Isotopic Stage (MIS) 5.5), the next to last interglacial (MIS 7.5), the third from last interglacial (MIS 9.3) and the fourth from last interglacial (MIS 11.3). The other sections were chosen from the last four ice ages. The depth of the sections ranged from 126.73 m (which corresponds to an estimated age of 4640 years) to 3285 m, corresponding to an estimated age of 409,000 years. Further information is given in Table 1.

2.2. Core decontamination

Each core section was decontaminated using the method described by Candelone et al. [11], in which the core section is held in a polyethylene lathe and mechanically chiselled using acid cleaned stainless steel knives. Various improvements were however made compared with the original procedure: up to seven concentric layers (of about 5 mm), were successively removed prior to collection of the inner part of the core and improved cleaning procedures were used for the preparation of the equipment used during the whole operation.

2.3. ICP-SFMS determinations

Each concentric layer and inner core were analysed separately in special clean laboratories. Li, V, Cr, Mn, Co, As, Rb, Sr, Ba, Bi and U were determined by ICP-SFMS using an Element2 instrument from Thermo Electron Corporation (Bremen, Germany) using a micro-flow (<100 μl min^{-1}) PFA nebulisation system that allowed us to analyse only a few milliliters of the melted samples [12]. Each melted sample aliquot was analysed directly, at least 24 h after acidification (with HNO_3 Ultrapure, Romil, Cambridge, UK) to pH 1. Since the trace elements present in a silicate matrix require digestion with hydrofluoric acid and other strong acids for complete dissolution, the fraction of the elements measured by ICP-MS after acidification, clearly does not represent the total content of the element in the ice matrix. The total element content was determined in some selected aliquots, from both glacial and interglacial periods, after digestion with ultrapure nitric and hydrofluoric acid, with microwave irradiation. The results show that different elements have a different behaviour. As an example, the fraction of Mn determined after acidification with HNO_3 at pH 1 corresponds to the total element content, while only from ~50% to ~65% of Ba is determined in the ice samples, depending on the age of the ice.

Table 1
Trace elements concentration (in pg/g) measured in 37 sections of the 3623 m Vostok ice core, Antarctica

Depth[a] (m)	Estimated age (yr BP)	Trace element concentrations (pg/g)											
		Al[b]	Li	V	Cr	Mn	Co	As	Rb	Sr	Ba	Bi	U
126.73	4640	1.8	4	2	<3.1	14	1.6	3	3.2	63	11	–	0.15
150.45	5750	3.7	9	3	<4.1	18	1.1	4	4	81	12	0.08	0.1
193.90	7845	5.8	10	3	11	28	1	2	6	88	15	0.31	0.5
513.00	30200	39.9	45	22	14	250	4.5	7	53	467	183	0.54	2
938.10	65080	120.0	96	82	30	552	11	16	115	740	429	0.8	3.1
948.00	66045	145.0	68	72	30	883	19	32	63	510	318	0.63	2.4
1050.00	75065	11.1	11	8	6	77	2.5	1	11	136	33	0.10	0.3
1205.68	86500	5.0	12	3	7.1	57	2.2	2	7	108	24	0.17	0.5
1353.50	97145	6.6	5	2	<4	42	1.0	3	6.3	115	17	0.08	0.10
1514.45	108400	40.0	29	9	11	201	1.9	8	24	188	70	0.36	0.7
1651.40	118500	4.1	4	1.5	<2	17	0.5	2	3.6	60	10	0.07	0.06
1815.45	127800	7.0	1	4	<4	37	2.3	5	3	43	16	–	0.4
1879.78	131200	2.0	<1	3	<5	14	1.1	<1	1.5	35	4.5	0.04	0.10
1917.45	133950	17.0	16	15	17	116	2	7	16	216	55	0.27	0.4
1999.00	142500	139.0	102	80	29	638	14	20	107	926	466	0.9	4
2078.60	151300	55.0	46	29	15	255	6	13	48	378	200	0.47	1.2
2199.40	165150	77.0	68	41	27	387	8	16	72	625	314	1.0	1.9
2252.40	171520	57.7	40	36	22	407	8	17	38	363	157	0.40	1.3
2378.40	187770	59.0	60	53	23	294	5.2	12	52	403	229	0.8	1.3
2504.50	203100	4.0	3	3	6	30	2.2	4	5	61	15	–	0.1
2534.00	206630	7.0	21	9	14	95	1.9	3	11	121	34	0.27	0.3
2616.00	216400	5.0	4	6	7	63	2.3	4	7	79	23	–	0.11
2682.40	226250	9.0	17	13	21	119	1.9	3	14	158	45	0.3	0.2
2751.00	237280	6.0	5	6	9	60	2.5	4	8	70	30	–	0.2
2770.40	239500	4.6	1	2.0	<2	32	0.6	2	4.2	80	13	0.08	0.1
2816.36	248450	47.9	26	31	19	455	8	11	28	387	147	0.21	1.0
2848.68	255400	79.1	41	63	28	598	12	15	46	319	186	0.30	1.2
2870.00	260800	186.0	97	121	53	1297	26	34	105	622	475	0.9	3
2886.00	265055	80.7	52	40	25	773	13	17	40	352	226	–	–
2984.00	289270	17.5	16	9	7	172	3.0	8	12	151	68	0.99	0.27
3059.00	309650	4.7	4	2	2.6	31	0.8	2	2.8	68	17	0.08	0.07
3107.01	321785	4.0	2.6	2	2.7	24	0.6	1	2.0	19	15	0.03	0.06
3149.01	335100	104.0	49	61	29	890	16	1	48	384	239	0.25	1.2
3184.92	353275	111.0	53	–	–	–	–	–	–	481	279	0.35	1.5
3223.99	374480	16.3	14	14	8	159	3.3	7	13	132	56	0.10	0.32
3263.00	397255	4.8	3.4	2.5	<3	30	1.0	1	2.7	67	17	0.05	0.06
3284.95	408990	2.1	2.3	2	<2	17	0.6	1	2	39	10.9	0.03	0.05

[a] Depth of the bottom of the core section.

[b] Concentration in ng/g.

Thanks to the possibility of working at three different resolution modes ($m/\Delta m = 400$, low resolution mode, LR; $m/\Delta m = 4000$, medium resolution mode, MR; $m/\Delta m = 10{,}000$, high resolution mode, HR), all of the analyte peaks could be physically resolved from spectroscopic interferences that can potentially hamper their accurate determination [12]. During the present work the LR mode was used for the analysis of Li, Rb, Sr, Ba, Bi and U, while the MR mode was preferred during the analysis of V, Cr, Mn and Co. As an example vanadium was analysed on mass 51 (abundance 99.75%); at this mass $^{35}Cl^{16}O$, $^{37}Cl^{14}N$, $^{34}S^{16}OH$ and $^{40}Ar^{11}B$ are physically resolved thanks to the high resolution achieved in MRM. Also, the possible formation of non-resolved interferences deriving from doubly charged ions such as $^{102}Pd^{2+}$ and $^{102}Ru^{2+}$ does not seem to be critical, because of the very low concentrations of these elements in the samples and the very low formation of doubly charged ions (MO+/M+ = 0.0009 − 0.0026). Furthermore, oxide formation for these metals is very low. It appears therefore that these interferences can be ignored.

Arsenic was analysed by taking advantage of the highest resolution (HR, $m/\Delta m = 10{,}000$) of the sector field mass spectrometer to resolve the interference of $^{40}Ar^{35}Cl$ on ^{75}As. Taking advantage of the high resolving power of the ICP-SFMS, all the possible interferences were therefore physically separated in the mass spectrometer and not hampered the accurate determination of trace elements in the ice core samples.

2.4. Blanks, precision and detection limits

Experimental blanks for the whole analytical procedure were determined by processing an artificial ice core prepared by freezing ultra-clean water [13]. Blanks were found to be negligible for all the metals except Cr, for which a slight contamination, due to the Cr rich stainless steel knives, was observed at the picogram per gram level. Therefore Cr concentrations at the low pg/g level must be considered as an upper limit of the genuine concentration. However high Cr glacial concentrations are probably only negligibly affected by this slight contamination and was found to be in the range of the instrumental standard deviation. The overall precision of the data was found to range from 2% for Sr to 15% for As at the lowest level of sample concentrations during interglacial periods. Detection limits expressed in pg/g were as follows: Li (1), V (0.4), Cr (1), Mn (0.3), Co (0.5), As (1), Rb (0.5), Sr (5), Ba (2), Bi (0.02) and U (0.01).

2.5. Reliability of the data

We established radial profiles of the variations of concentration for the different metals from the outside to the inside of the cores, to make sure that the concentrations measured in the inner part were obtained after the decontamination was completed, and therefore represented the original concentration in the ice, free from any contamination.

As an example, typical profiles obtained for U, Co, As and Mn for the 1879.78 m section (age of 131,200 yr. BP, which corresponds to interglacial stage 5.5 characterised by extremely low concentration in the ice) are shown in Fig. 2. The profiles shown in the figure do not include the data for the most contaminated outside layer, as this was not analysed because such high concentrations would have contaminated the sample introduction system of the ICP-SFMS instrument. It can be seen that the concentration values reach well established plateau values in all four cases, despite the fact that the 1879.78 m section corresponds to interglacial ice with extremely low concentration values. It indicates that the concentrations measured in the inner core represent the metal concentration in the pristine ice.

3. Results and discussion

3.1. Changes in concentrations and fluxes during the last four climatic cycles

Concentrations measured in the innermost part of the 37 sections are given in Table 1. They are the first data ever published on past variations of these different elements in Antarctic ice during the last four climatic cycles. Concentrations range from 0.03 pg/g for Bi in the 3284.95 m section to 1.3 ng/g for Mn in the 2870.0 m section.

Pronounced variations in concentrations are observed for all the elements over the ~410,000 years time period covered by our samples. For instance the highest concentrations measured for V (121 pg/g) are about 80 times higher than the lowest (1.5 pg/g). The variations appear to be firmly linked to climatic conditions. Their maximum amplitudes however, vary greatly from one element to another. The highest amplitude is for Li (max/min = 102), the lowest is for Cr (max/min = 20). Concentrations of most elements were very low during the warm periods, characterised by less negative δD values (Fig. 1). Conversely, much higher trace element concentrations are observed during cold periods, characterised by more negative δD values (Fig. 1). As an illustration, Fig. 1 shows the variations observed for Li, Co, Rb and U.

Fallout fluxes were calculated for each element by combining the concentrations measured in the ice with the yearly ice accumulation rate at each depth [9,14]. The ice accumulation rate at Vostok has varied by a factor of ~2 during the last two climatic cycles, with lowest values during the cold climatic stages when concentrations of the elements considered in our work

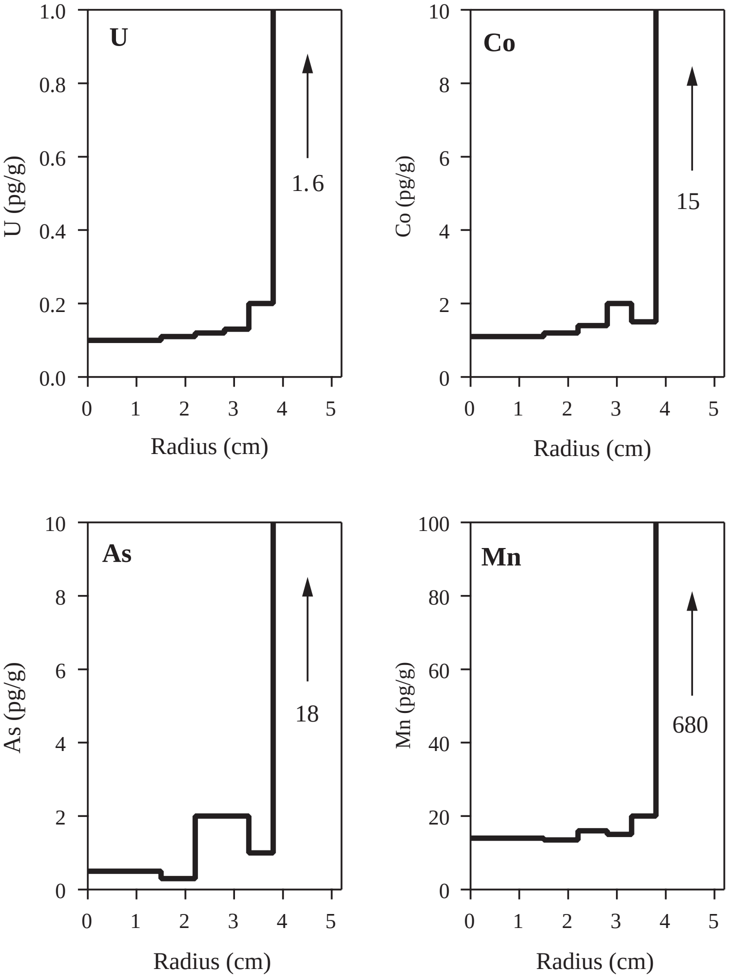

Fig. 2. Changes in U, Co, As and Mn concentrations as a function of radius in the 1879.78 m ice core section (131,200 years BP).

are at a maximum. Taking that into account, changes in fallout fluxes closely parallel changes in concentrations, but with a smaller amplitude.

3.2. Crustal enrichment factors (EF_c)

Rock and soil dust is a major source of trace elements in the atmosphere [15]. In order to assess the importance of the rock and soil dust contribution in Vostok ice during the last four climatic cycles, we calculated crustal enrichment factors (EF_c) for each element and depth. EF_c is defined as the concentration ratio of a given element to that of Al (which is a good proxy for rock and soil dust; Al concentrations were determined in each section by graphite furnace atomic absorption spectrometry [16]) in the ice, normalised to the same concentration ratio characteristic of the upper continental crust. For example, the EF_c for Co is thus:

$$EF_c = \frac{[Co]_{ice}/[Al]_{ice}}{[Co]_{crust}/[Al]_{crust}}$$

We have used here the data for the upper continental crust given by Wedepohl [17]. It should however be emphasised that the choice of other crustal compositions, for instance that given by Rudnick and Fountain [18], would not make any significant differences in the interpretation. Despite the fact that the composition of rock and soil dust reaching Antarctica might significantly differ from the composition of the mean upper crust, EF_c values close to unity (up to ~5) will indicate that the corresponding elements mainly originate from rock and soil dust. Conversely, values significantly larger than unity will most likely indicate a significant contribution from other natural sources.

EF_c values calculated for the 37 sections are given in Table 2. When looking at the values obtained for the different elements and their variations during the last four climatic cycles, the elements considered in our study can be separated into several groups.

The first group consists of V, Mn, Rb, Ba and U; these are elements for which the EF_c values are close to the unity, whatever the period (see Table 2). This is illustrated in Fig. 3 for Mn. These EF_c values show that the atmospheric cycle of these five elements in the remote polar area of the Southern Hemisphere was dominated by crustal dust, both during glacial and interglacial periods. They also indicate that V, Mn, Rb, Ba and U could eventually substitute Al as a crustal reference element in Antarctic ice during the preceding climatic cycles.

Table 2
Crustal enrichment factors in 37 sections of the 3623 m Vostok ice core, Antarctica

Depth[a] (m)	Estimated age (yr BP)	Crustal enrichment factor										
		Li	V	Cr	Mn	Co	As	Rb	Sr	Ba	Bi	U
126.73	4640	9	1.4	3.8	1.1	5.8	70	1.2	9	0.7	–	2.5
150.45	5750	9	1.0	2.4	0.7	1.9	37	0.8	5	0.4	13	1.2
193.90	7845	6	0.7	4.4	0.7	1.3	16	0.7	4	0.3	34	2.7
513.00	30200	4	0.8	0.8	0.9	0.7	7	0.9	3	0.5	8	1.4
938.10	65080	3	1.0	0.5	0.7	0.6	5	0.7	2	0.4	4	0.8
948.00	66045	2	0.7	0.5	0.9	0.9	8	0.3	1	0.3	3	0.5
1050.00	75065	3	1.1	1.2	1.0	1.5	3	0.7	3	0.3	6	0.8
1205.68	86500	9	0.9	3.1	1.7	3.0	15	1.0	5	0.6	22	3.2
1353.50	97145	2	0.5	1.4	0.9	1.0	17	0.7	4	0.3	8	0.5
1514.45	108400	3	0.3	0.6	0.7	0.3	8	0.4	1	0.2	6	0.5
1651.40	118500	4	0.5	1.1	0.6	0.9	17	0.6	4	0.3	11	0.4
1815.45	127800	0.4	0.8	1.3	0.8	2.2	26	0.3	2	0.3	–	1.6
1879.78	131200	–	2.0	5.8	1.0	3.5	–	0.5	4	0.3	13	1.6
1917.45	133950	3	1.3	2.2	1.0	0.9	16	0.7	3	0.4	10	0.8
1999.00	142500	3	0.8	0.5	0.7	0.6	6	0.5	2	0.4	4	0.9
2078.60	151300	3	0.8	0.6	0.7	0.7	9	0.6	2	0.4	5	0.7
2199.40	165150	3	0.8	0.8	0.7	0.7	8	0.7	2	0.5	8	0.8
2252.40	171520	2	0.9	0.8	1.0	0.9	11	0.5	2	0.3	4	0.7
2378.40	187770	4	1.3	0.9	0.7	0.6	8	0.6	2	0.4	8	0.7
2504.50	203100	2	1.0	3.4	1.1	3.7	35	0.9	4	0.4	–	1.0
2534.00	206630	11	1.9	4.3	2.0	1.8	16	1.1	4	0.6	25	1.2
2616.00	216400	3	1.6	3.3	1.8	3.1	31	1.0	4	0.5	–	0.7
2682.40	226250	7	2.1	5.0	1.9	1.4	11	1.1	4	0.6	22	0.7
2751.00	237280	3	1.4	3.4	1.5	2.8	28	0.9	3	0.6	–	1.0
2770.40	239500	1	0.6	1.2	1.0	0.9	15	0.6	4	0.3	10	0.8
2816.36	248450	2	0.9	0.9	1.4	1.2	9	0.4	2	0.4	3	0.6
2848.68	255400	2	1.2	0.8	1.1	1.0	7	0.4	1	0.3	2	0.5
2870.00	260800	2	0.9	0.6	1.0	0.9	7	0.4	1	0.3	3	0.6
2886.00	265055	2	0.7	0.7	1.4	1.1	8	0.4	1	0.3	–	–
2984.00	289270	3	0.7	0.9	1.4	1.1	18	0.5	2	0.4	36	0.5
3059.00	309650	3	0.6	1.2	1.0	1.2	16	0.4	4	0.4	11	0.5
3107.01	321785	2	0.6	1.5	0.9	0.9	12	0.4	1	0.4	5	0.5
3149.01	335100	2	0.9	0.6	1.3	1.0	0.2	0.3	1	0.3	1	0.4
3184.92	353275	2	–	–	–	–	–	–	1	0.3	2	0.4
3223.99	374480	3	1.2	1.1	1.4	1.4	16	0.6	2	0.4	4	0.6
3263.00	397255	3	0.8	1.5	0.9	1.4	7	0.4	3	0.4	6	0.4
3284.95	408990	4	1.3	2.4	1.2	1.9	20	0.5	4	0.6	8	0.7

[a] Depth of the bottom of the core section.

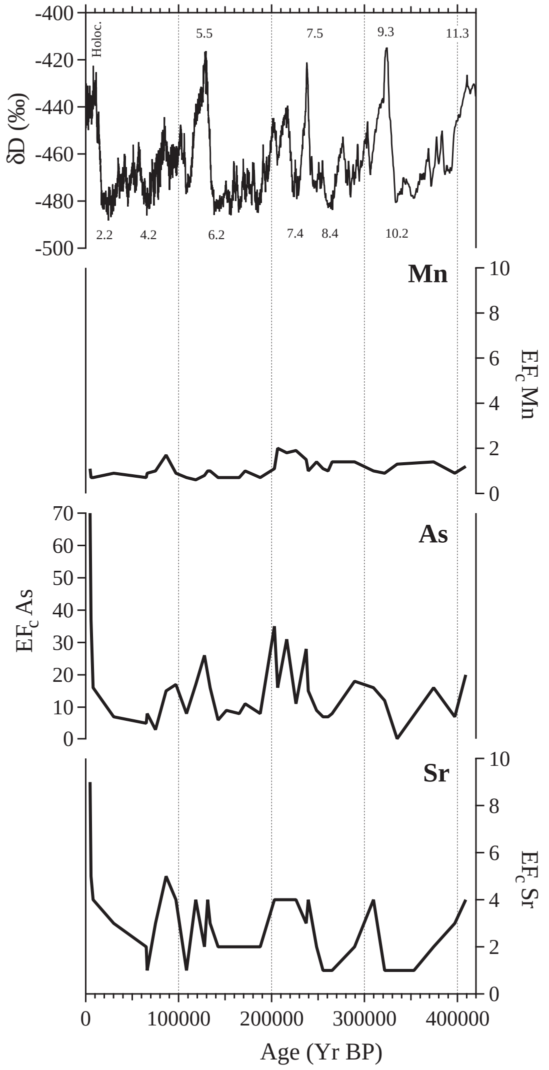

Fig. 3. Vostok Antarctic ice core: changes in crustal enrichment factors (EF$_c$) for Mn, As and Sr as a function of the age of the ice during the last four climatic cycles (the past 410,000 years). Also shown at the top of the figure is the deuterium profile from Petit et al. [9], with MIS numbers from Bassinot et al. [10].

A second group of elements is composed of Li, Cr, Co and Sr. For these elements, low EF$_c$ values are observed in some of the sections, while moderately elevated values are observed in other sections (Table 2). As illustrated in Fig. 3 by Sr, the lowest values are generally observed during the coldest periods, while the higher values occurred during interglacial periods. The atmospheric cycles of Li, Co and Sr were dominated by crustal dust during the coldest stages, while the influence of additional sources was probably important during warmer periods. Some of the observed changes may however also be linked with changes in rock and soil dust source areas, soil physical conditions (variations in humidity), or transport processes (settling) between glacial and interglacial periods [19,20].

Arsenic and Bi are, however, special cases. EF$_c$ values close to unity are indeed rarely observed for these elements (Table 2). The lowest values are observed during the coldest climatic stages, while the higher values are observed during the warm stages, Fig. 3. The moderate values during the coldest stages indicate that inputs from sources other than dust were probably significant even during these periods. Alternatively, they could be linked with changes in the composition of crustal dust reaching Antarctica, with an enrichment in As and Bi in rock and soil from Patagonia, which is a dominant source area for dust during the coldest climatic stages [4,21,22]. The rather high values recorded during the warm periods show that in all likelihood the atmospheric cycles of As and Bi in the remote polar area of the Southern Hemisphere were dominated by sources other than rock and soil dust during these periods.

3.3. Contributions from sea salt and volcanoes

Besides rock and soil dust, other important sources of atmospheric trace elements are sea salt spray, volcanic emissions and continental and marine biogenic emissions [15].

The contribution from sea salt spray was evaluated from Na concentrations measured in the ice [16] (after correction for the Na contribution from rock and soil dust) and the elemental ratios in ocean water [23,24]. These ratios were not combined with possible enrichments found in sea-derived aerosols relative to seawater, from when marine aerosol is formed by bubble bursting through the sea surface micro layer, because recent studies have cast some doubt on the values of these possible enrichments [25].

The contribution from sea salt was found to be important for Sr, especially during interglacial periods (about 40%) and to a lesser extent during cold periods (about 20%). The contribution from sea salt is negligible for all the other elements, whatever the period.

A rough estimate of the contribution from volcanoes was made from the concentration of non-sea-salt sulfate (nss-SO_4) in the ice [16], by assuming that ~10 – 15% of nss-SO_4 originates from volcanoes [2]. This was combined with the most recent estimates available of element/S ratios in volcanic emissions [15,26]. It must however be emphasized that such estimates are rather crude, especially because of the large variations in published elements/S ratios in volcanic emissions. The As/S mass ratio (maximum value of 1.5×10^{-4}) given for worldwide volcanic emissions by Nriagu [15] is five times higher than the same ratio (0.3×10^{-4}) for these emissions given by Hinkley and his co-workers [26]. Also estimates of element/S ratios in volcanic emissions are not available for several of the elements considered in this work. The calculation shows that volcanic emissions were possibly a significant source for As and Bi during warm periods. However, such a contribution cannot entirely explain the high EF_c values observed for As during warm climatic stages. In contrast, the volcanic contribution calculated for Bi would imply concentrations in the order 1 pg/g, whereas concentrations found in Vostok ice are in general much lower. However this calculation suggests a possible strong volcanic contribution for Bi.

A possible local source within Antarctica could be Mount Erebus, a volcano that is located ~1100 km from Vostok. Zreda-Gostynska and co-workers [27] have indeed shown that Erebus is a significant source of various trace elements to the Antarctic atmosphere. They made a rough estimate of the potential contribution of Mt. Erebus to the trace elements content of East Antarctic snow assuming homogeneous fallout over the whole continent. When compared with the concentrations we find in Vostok ice, it appears that Mt. Erebus could be a significant contributor to the fallout of several heavy metals, especially during warm periods. It must however be kept in mind that the data by Zreda-Gostynska and co-workers derive only from short sampling periods between 1986 and 1991. It might not then be applicable to the ~410,000 years period covered by our samples. In addition, it is likely that fallout from Erebus volcano is not evenly deposited over the Antarctic continent. It thus makes it difficult to perform any quantitative estimate of the possible contribution from Mt. Erebus (or other Antarctic volcanoes).

Finally, our data do not allow any estimate of the contributions from continental marine biogenic activity to be made. Such contributions cannot however be neglected, as illustrated for instance by recent studies of the production of methylated metals by polar marine bacteria [28,29].

3.4. Trace elements vs climate relationship

Concentrations of trace elements in Vostok ice remain very low for δD values between – 420 and – 470‰, but show a sharp increase when δD values

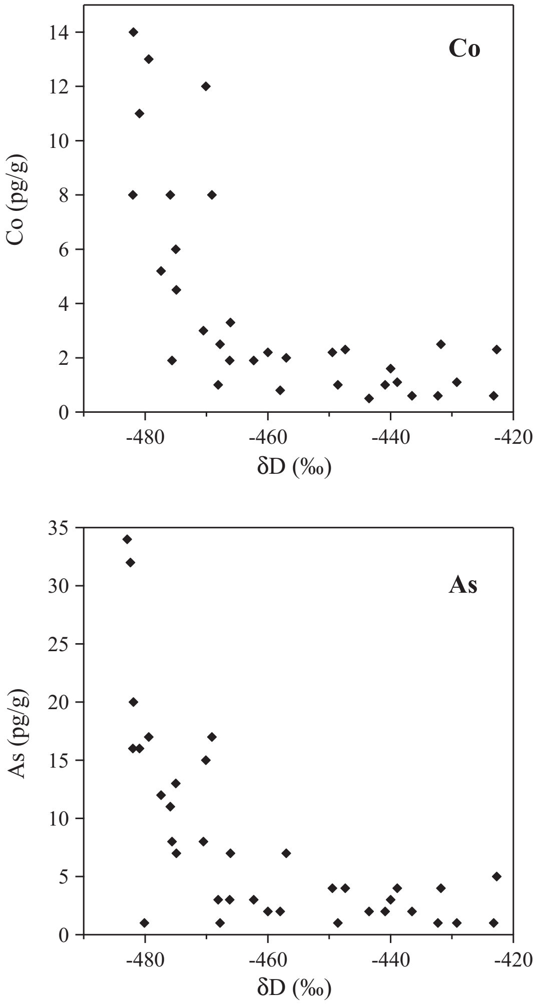

Fig. 4. Vostok Antarctic ice core: changes in concentrations of Co and As a function of the deuterium content of the ice (expressed in per mil δ units).

fall below −470‰. This is illustrated in Fig. 4 for Co and As. This observation suggests that there is a critical point in the climate mechanism beyond which the fallout of trace elements to the Antarctic plateau is activated and the deposition is enhanced. The main inputs of trace elements to the Antarctic ice cap could have been driven by large changes in wind strength, which occurred when a critical temperature gradient between low and high latitudes was reached, allowing larger amounts of trace metals to be carried by dust to Antarctica. A transport activation could be also related to fast changes in local conditions of the source areas from which the trace elements originated [20]. For instance, a variation in the humidity of dust source areas such as Patagonia [19] could have resulted in a different amount of dust suspended and transported by wind circulation to the Antarctic plateau, therefore enhancing the fallout of trace elements.

4. Conclusion

Our work has documented large natural changes in the occurrence of various trace elements in Antarctic ice over the last four climatic cycles, highlighting important changes in the atmospheric cycles of trace elements in the remote polar areas of the Southern Hemisphere in parallel with climate.

It will now be important to extend this study to the preceding climatic cycles within the new EPICA Dome C ice core, and to include other trace elements such as Hg and Se, which could be valuable tracers of marine biogenic emissions, or Ir and Pt, which are good indicators of fallout of cosmic material.

Acknowledgements

The Vostok ice cores were obtained as part of a joint program between Russia, France and the USA. We thank the Russian Antarctic Expeditions, the Institut Polaire Paul Emile Victor and the Division of Polar Programs (NSF) for logistical support, and the drilling team from St. Petersburg Mining Institute for fieldwork. In Italy this study was performed within the framework of Projects on “Environmental Contamination” and “Glaciology and Paleoclimatology” of the Italian *Programma Nazionale di Ricerche in Antartide* and financially supported by ENEA through co-operation agreements with the Universities of Venice and Milan, respectively. In Korea, grants from the Korea Ocean Research and Development Institute (PP04105) and a National Research Laboratory program from the Ministry of Science and Technology (PN51200) supported this research. It was also supported in France by the Institut Universitaire de France, the Ministère de l′Environnement et de l′Aménagement du Territoire, the Agence de l′Environnement et de la Maîtrise de l′Energie, the Institut National des Sciences de l′Univers and the University Joseph Fourier of Grenoble. Finally we would like to thank Giulio Cozzi and Vania Gaspari for laboratory assistance, and Paul Vallelonga for the preparation of the artificial ice core.

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