

Climate-related variations in crustal trace elements in Dome C (East Antarctica) ice during the past 672 kyr

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Abstract Cr, Fe, Rb, Ba and U were determined by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) in various sections of the 3,270 m deep ice core recently drilled at Dome C on the high East Antarctic plateau as part of

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the EPICA program. The sections were dated from 263 kyr BP (depth of 2,368 m) to 672 kyr BP (depth of 3,062 m). When combined with the data previously obtained by Gabrielli and co-workers for the upper 2,193 m of the core, it gives a detailed record for these elements during a 672-kyr period from the Holocene back to Marine Isotopic Stage (MIS) 16.2. Concentrations and fallout fluxes of all elements are found to be highly variable with low values during the successive interglacial periods and much higher values during the coldest periods of the last eight climatic cycles. Crustal enrichment factors indicates that rock and soil dust is the dominant source for Fe, Rb, Ba and U whatever the period and for Cr during the glacial maxima. The relationship between Cr, Fe, Rb, Ba and U concentrations and the deuterium content of the ice appears to be similar before and after the Mid-Brunhes Event (MBE, around 430 kyr BP). Mean concentration values observed during the successive interglacials from the Holocene to MIS 15.5 appear to vary from one interglacial to another at least for part of the elements. Concentrations observed during the successive glacial maxima suggest a decreasing trend from the most recent glacial maxima (MIS 2.2 and 4.2) to the oldest glacial maxima such as MIS 14.2, 14.4 and 16.2, which could be linked with changes in the size distribution of dust particles transported from mid-latitude areas to the East Antarctic ice cap.

1 Introduction

Deep Antarctic ice cores have already provided a wealth of data on past climate related changes in the natural biogeochemical cycles of various trace elements. This was made possible by the recent recovery of exceptional deep ice cores such as the 3,623 m ice core drilled at Vostok station (Petit et al. 1999) and the 3,270 m ice core drilled at Dome C as part of the European EPICA program (EPICA Community members 2004), and the development of highly sophisticated ultra-clean and ultra-sensitive procedures to determine various trace elements down to extremely low concentrations levels in these cores (Ng and Patterson 1981; Boutron and Patterson 1986; Candelone et al. 1994; Gabrielli et al. 2006).

These procedures have allowed the analyses of various sections of the 3623 m Vostok ice core, which covers the last four climatic cycles [past ~ 420 kyr, back to the end of Marine Isotopic Stage (MIS) 11 (Bassinot et al. 1994)]. Concentrations of most trace elements are found to be highly variable, with generally low values during interglacial periods and warm interstadials and much higher values during the coldest stages of the last four ice ages (Hong et al. 2003, 2004, 2005; Gabrielli et al. 2005a).

Although the Vostok trace element records are the longest ones presently available, they cover only a rather limited time period. In particular, they do not provide a comprehensive view of the entire MIS 11, which emerges as a key interglacial period from about 390 to 420 kyr BP, possibly the best analogue to the present Holocene interglacial (Berger and Loutre 2003; Droxler et al. 2003). MIS 11 is an unusual and perhaps unique interglacial interval. It exhibited warm interglacial climatic conditions for an interval of at least 30 kyr, a duration twice as long as the most recent interglacial stages, with orbital parameters (low eccentricity and consequently weak precessional forcing) similar to those of the present. Moreover, the Vostok trace element record does not provide data for the period between the Mid-Pleistocene Revolution (MPR) (dated as 900 kyr BP; Raymo et al. 1997) and the

Mid-Brunhes event (MBE) (which roughly corresponds to the transition between MIS 12 and MIS 11 about 430 kyr BP; Berger and Wefer 2003). The period between MPR and MBE was characterized by less pronounced warmth in interglacial periods in Antarctica, but a higher proportion of each cycle was spent in the warm mode (EPICA Community members 2004).

We present here comprehensive data on past changes in the occurrence of various trace elements (Cr, Fe, Rb, Ba and U) in Antarctic ice during the period from 263 kyr BP (MIS 8.2) to 672 kyr BP (MIS 16.2). These are elements which mainly derive from the continental crust. The data were obtained by analysing various sections of the 3,270 m deep ice core recently obtained at Dome C as part of the European EPICA program, using ultra-clean decontamination procedures and the highly sensitive inductively coupled plasma sector field mass spectrometry (ICP-SFMS) technique. The sections which were analysed include various sections dated from MIS 11, together with sections dated from before and after the Mid-Brunhes Event.

2 Experimental

2.1 Description of the ice samples

The 78 ice samples, considered in this study, derive from 39 core sections from the 3,270 m deep ice core recently drilled at Dome C (75°06' S; 123°21' E, altitude 3233 m, mean annual temperature—54°C) on the East Antarctic plateau as part of the European Project for Ice Coring in Antarctica (EPICA; EPICA Community members 2004). The core was electromechanically drilled from 1999 to January 2005 in a fluid-filled hole. The depth of the 78 samples ranged from 2,368.6 to 3,061.8 m (Appendix A).

Age dating of the ice is based on the new official EDC3Beta6 chronology (Parrenin et al. 2007). It combines a glaciological mechanical ice flow model, and a set of independent age markers all along the core. These markers were obtained by pattern matching of recorded parameters to either absolutely dated paleoclimatic records or to insolation variations.

It shows that the ice at 2,368.6 m is dated at 263 kyr BP which corresponds to MIS 8.2, while the ice at 3061.9 m is dated at 672 kyr which corresponds to MIS 16.2. Our samples thus cover a ~400 kyr time period from MIS 16.2 to MIS 8.2.

2.2 Ice core decontamination and preparation

Each of the 39 core sections (length of about 55 cm) was mechanically decontaminated in order to remove the outside of the core which was heavily contaminated during drilling operations in the field. It involved chiselling successive veneer layers of ice in progression from the contaminated outside towards the pristine central part of each section, inside a laminar flow clean bench at -15°C, using ultra-clean procedures which have been described in details elsewhere (Candelone et al. 1994; Hong et al. 2005). It yielded the innermost part of each core section, which was then divided into three consecutive parts: (1) a 5 cm long part at the bottom of the section for the subsequent determination of Hg; (2) two consecutive 20 cm long parts, which were used for the present study giving the 78 depth intervals listed in Appendix A.

In order to check the efficiency of the decontamination, changes in the concentration of each element from the outside to the inside of the sections were investigated. Good plateaus of concentration were observed in the central part of the cores in all cases, therefore representing the original concentration in the ice. This is illustrated in Fig. 1 for Ba and Cr in the 2,776.1 m section (dated at 425 kyr BP, which corresponds to the MIS 11 interglacial period) and for Ba and Cr in the 3,040.1 m section (dated at 633 kyr, which corresponds to the MIS 16 glacial period).

Each central part was melted at room temperature in ultra-clean wide mouth low-density polyethylene (LDPE) 1 l bottles inside a clean laboratory (Boutron 1990). 10 ml aliquots were then taken inside ultra-clean 15 ml LDPE bottles and kept frozen until analysis.

2.3 Mass spectrometry and calibration

All samples were analysed at the Department of Environmental Sciences (DES) in Venice by inductively coupled plasma sector field mass spectrometry (ICP-SFMS)

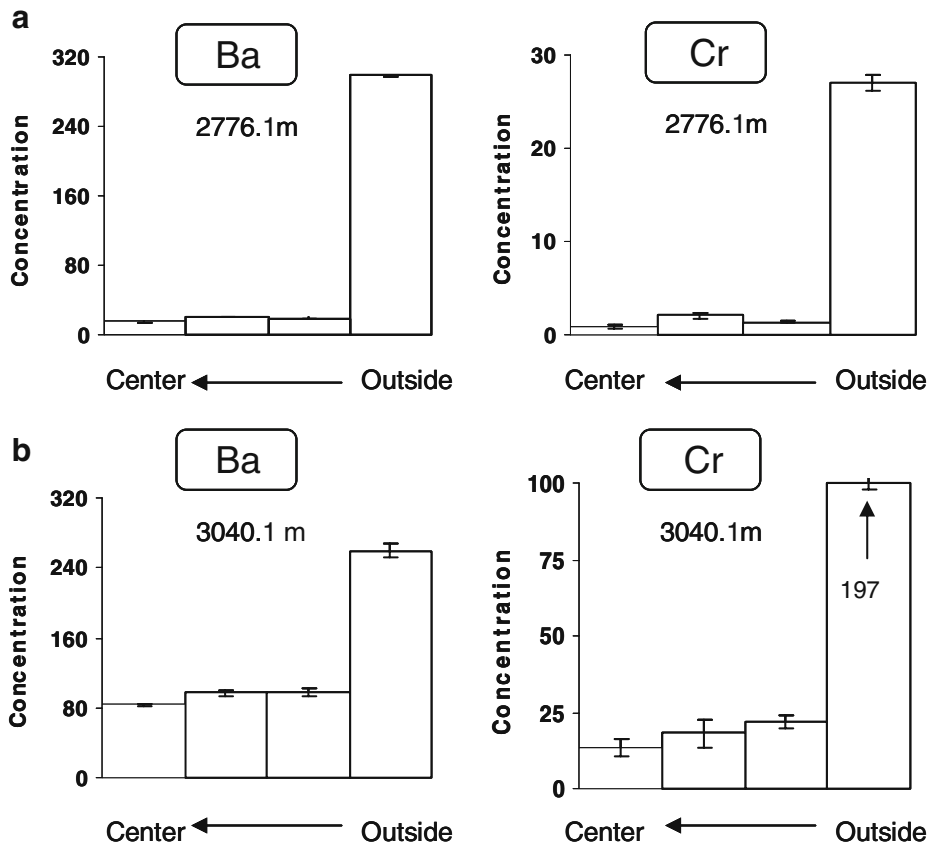


Fig. 1 EPICA/Dome C Antarctic ice core: changes in concentrations of Ba and Cr from the outside towards the center in two core sections: **a** depth of 2,776.1 m (425 kyr BP; MIS 11.3 interglacial); **b** depth of 3,040.1 m (633 kyr; MIS 16.2 glacial maximum). All concentrations are expressed in pg/g

using an Element2 instrument from Thermo Fisher (Bremen, Germany) equipped with a micro-flow ($<100 \mu\text{l min}^{-1}$) PFA nebulisation system (Planchon et al. 2001). By working at three different resolution modes ($m/\Delta m = 400$, low resolution mode LR; $m/\Delta m = 4,000$, medium resolution mode MR; $m/\Delta m = 10,000$, high resolution mode HR), most of the analyte peaks can be physically resolved from spectroscopic interferences that potentially hamper their accurate determination. LR mode was used for the determination of Rb, Ba and U while the MR mode was preferred for Cr and Fe.

The external calibration curve method was used for the quantification of the analytes. Calibration standard solutions were analysed at the beginning and at the end of the measurement session. Usually, standards were prepared by dilution using ultrapure water in ultraclean LDPE bottles, acidified using double distilled ultrapure HNO_3 from Curtin University of Technology, Perth, Australia, (Vallelonga et al. 2002) to make a 1% solution.

In order to make sure that the changing amount of dust in the ice could not bias the calibration of the instrument, several different sets of standard solutions were also prepared by dilution using melted Antarctic ice dated from glacial periods (rather high dust content) and interglacial periods (low dust content). The only two elements for which significant effects were observed are Fe (up to 60%) and U (up to 20%; see Appendix C). It shows that when using standards prepared with laboratory ultrapure water, U concentrations are under-estimated for interglacial periods while Fe concentration are overestimated whatever the period. A systematic correction was then applied for these two elements (see Appendix C).

Detection limits ranged from 0.02 pg/g for U to 40 pg/g for Fe. Overall procedural blanks were determined by processing an artificial ice core, made by freezing ultrapure water in which the concentrations of the different elements were known beforehand (Vallelonga et al. 2002). The corresponding contribution was found to be extremely small. Typical precisions in terms of relative standard deviations were found to range from 5% for Ba and Rb to 30% for U (see Appendix A).

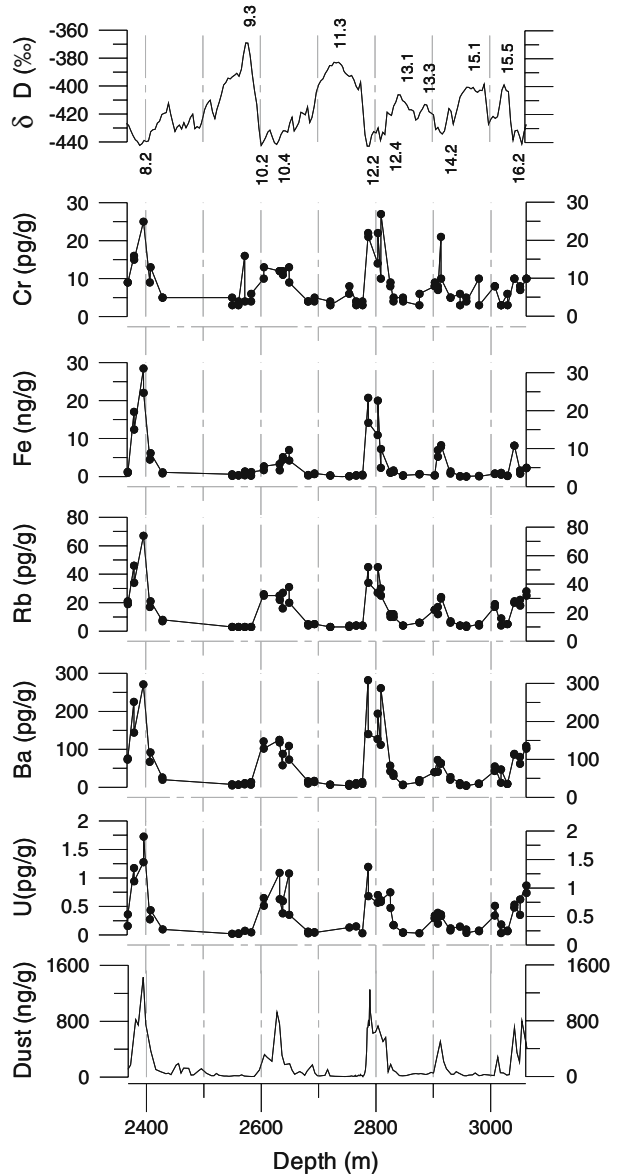
3 Results and discussion

3.1 Concentrations in Antarctic ice dated back to 672 kyr BP

Concentrations measured in the 78 samples are listed in Appendix A. Changes in concentrations as a function of the depth of the ice are shown in Fig. 2, together with changes in the deuterium content of the ice (expressed in δD per mil). Pronounced variations in concentrations are observed for all elements from MIS 8.2 to MIS 16.2, with high concentrations values during the coldest climatic stages and low concentrations values during interglacial periods.

For Cr, Rb and Ba, our data can be combined with the data previously obtained by Gabrielli et al. (2005b) and Vallelonga et al. (2005) for the upper 2,193 m of the EPICA Dome C ice core (ice dated from 0.5 to 217 kyr BP), giving comprehensive time series for these three elements over a ~ 672 kyr period from the Holocene to MIS 16.2, Fig. 3 and Table 1. Along this 672 kyr period, concentrations of these three elements are found to strongly vary as a function of δD . However, the earlier period was characterized by less pronounced variations, excepting Cr, see Fig. 3.

Fig. 2 EPICA/Dome C Antarctic ice core: changes in concentrations of Cr, Fe, Rb, Ba and U as a function of depth from 2,368.6 to 3,061.9 m (263 to 672 kyr BP). Also shown at the top of the figure are the variations in deuterium concentrations (expressed in delta per mil; EPICA community members 2004), Marine Isotopic Stages (MIS) numbers (Bassinot et al. 1994) and at the bottom of the figure changes in dust concentrations (EPICA community members 2004)



It is the first time natural variations have been observed over such a long time period with such high sampling frequency. The only other data covering long periods of time were obtained from the analyses of the Vostok ice core and for the EPICA Dome C, for iron (Wolff et al. 2006). However, they covered only 420 kyr, and only part of MIS 11. Other studies are few and deal with much shorter time periods, Table 1.

Fallout fluxes were calculated for each element by combining concentrations measured in the ice (data from this work for the period from 263 to 672 kyr BP; data from Gabrielli et al. (2005b) for the period from 0.5 to 217 kyr BP) at each

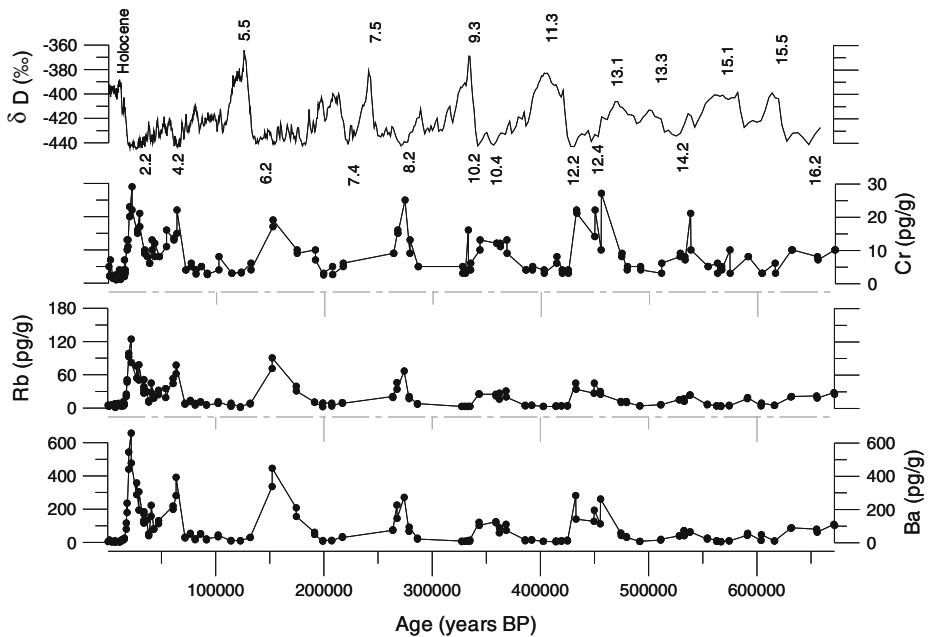


Fig. 3 EPICA/Dome C Antarctic ice core: changes in concentrations of Cr, Rb and Ba during the past 672 kyr (EDC3Beta6 timescale from Parrenin et al. 2007). Data for the period from 0.5 to 220 kyr BP from Gabrielli et al. (2005b). Also shown at the top of the figure are changes in deuterium concentrations and MIS numbers (EPICA community members 2004). All concentrations are expressed in pg/g, except for deuterium (delta per mil)

depth with the estimated yearly ice accumulation rate at that depth (expressed in $\text{g H}_2\text{O cm}^{-2} \text{ year}^{-1}$). The ice accumulation rate at Dome C has varied by a factor ~ 2 between very cold climatic stages ($\sim 1.3 \text{ g H}_2\text{O cm}^{-2} \text{ year}^{-1}$) and interglacial periods ($\sim 2.7 \text{ g H}_2\text{O cm}^{-2} \text{ year}^{-1}$) (EPICA community members 2004). Changes in fallout fluxes are found to match very well changes in concentrations. The ratio between the highest and the lowest fluxes is however about half of the corresponding ratio of the concentrations since the accumulation rate is lower during the coldest stages when concentrations are maximum.

3.2 Comparison between Vostok and Dome C for the past 420 kyr

Present day snow accumulation rates at Dome C ($\sim 2.7 \text{ g H}_2\text{O cm}^{-2} \text{ year}^{-1}$) and Vostok ($\sim 3 \text{ g H}_2\text{O cm}^{-2} \text{ year}^{-1}$) are very similar. They have varied by a factor ~ 2 between glacial maxima and interglacial periods (Petit et al. 1999; EPICA Community members 2004). It is therefore possible to compare the data obtained at the two locations. For instance, Fig. 4 compares the Ba concentration profile previously obtained by Gabrielli et al. (2005a) for Vostok for the past 420 kyr with the profile obtained here for the same time interval. It can be seen that the two profiles are in excellent agreement. Especially, high Ba concentration values are observed at both locations for the glacial maxima. The Vostok and Dome C concentration profiles are also in very good agreement for the other metals which have been determined in both cores (Cr, Rb and U).

Table 1 East Antarctica: concentrations of various crustal trace elements in ice dated from interglacial and glacial maxima periods collected at Dome C, Vostok and Taylor Dome

Location	Age	Period	Measured concentration (pg/g)				
			Cr	Fe ^a	Rb	Ba	U
Dome C	0.5–217 kyr BP	Interglacial	7 ^b	0.07 ^c	1.2 ^b	2.1 ^b	0.01 ^d
		Glacial	29 ^b	64 ^c	124 ^b	657 ^b	6.6 ^d
Dome C ^e	263–430 kyr BP	Interglacial	3	0.1	3	4	0.02
		Glacial	29	28	67	271	1.7
Dome C ^e	430–670 kyr BP	Interglacial	3	0.1	3	4	0.03
		Glacial	48	21	45	282	1.2
Vostok ^f	4.6–420 kyr BP	Interglacial	2	–	1.5	4.5	0.05
		Glacial	53	–	115	475	4
Taylor Dome ^g	1.3–13 kyr BP 27.2 kyr BP	Interglacial	–	–	1.05	8.1	–
		Glacial	–	–	36.3	163	–

^aConcentrations expressed in ng/g

^bGabrielli et al. (2005b)

^cWolff et al. (2006)

^dV. Gaspari, personal communication

^eThis work

^fGabrielli et al. (2005a)

^gHinkley and Matsumoto (2001)

3.3 Crustal enrichment factors

In order to assess the importance of the rock and soil dust contribution for the five elements studied in this work, we have calculated the Crustal Enrichment Factor (EF_c) for each element with depth (Appendix B). EF_c is defined as the concentration ratio of a given element to that of Ba (which is a good proxy of continental dust) in the ice, normalized to the same concentration ratio characteristic of the upper continental crust (UCC). For example, the EF_c for Rb is thus:

$$EF_c(\text{Rb}) = \frac{[\text{Rb}]_{\text{ice}} / [\text{Ba}]_{\text{ice}}}{[\text{Rb}]_{\text{UCC}} / [\text{Ba}]_{\text{UCC}}}$$

We have used here the data for the upper continental crust given by Wedepohl (1995). It should however be mentioned that the use of other crustal compositions data, for instance those given by Rüdnick and Fountain (1995) would not make any significant difference to the interpretation. Despite the fact that the composition of rock and soil dust reaching Dome C might significantly differ from the composition of the mean upper continental crust, EF_c values close to unity (up to ~5) will indicate that the corresponding element mainly originated from the continental dust. Conversely, EF_c values much larger than unity will suggest a significant contribution from other natural sources.

As shown in Appendix B, EF_c values for Fe, Rb and U are found to be close to unity, whatever the period, showing that the atmospheric cycle of these elements in the remote areas of the Southern Hemisphere was dominated by crustal dust, both during glacial and interglacial periods. For these elements, the range of maximum to minimum concentrations is up to about 100. Interestingly, this is about the range

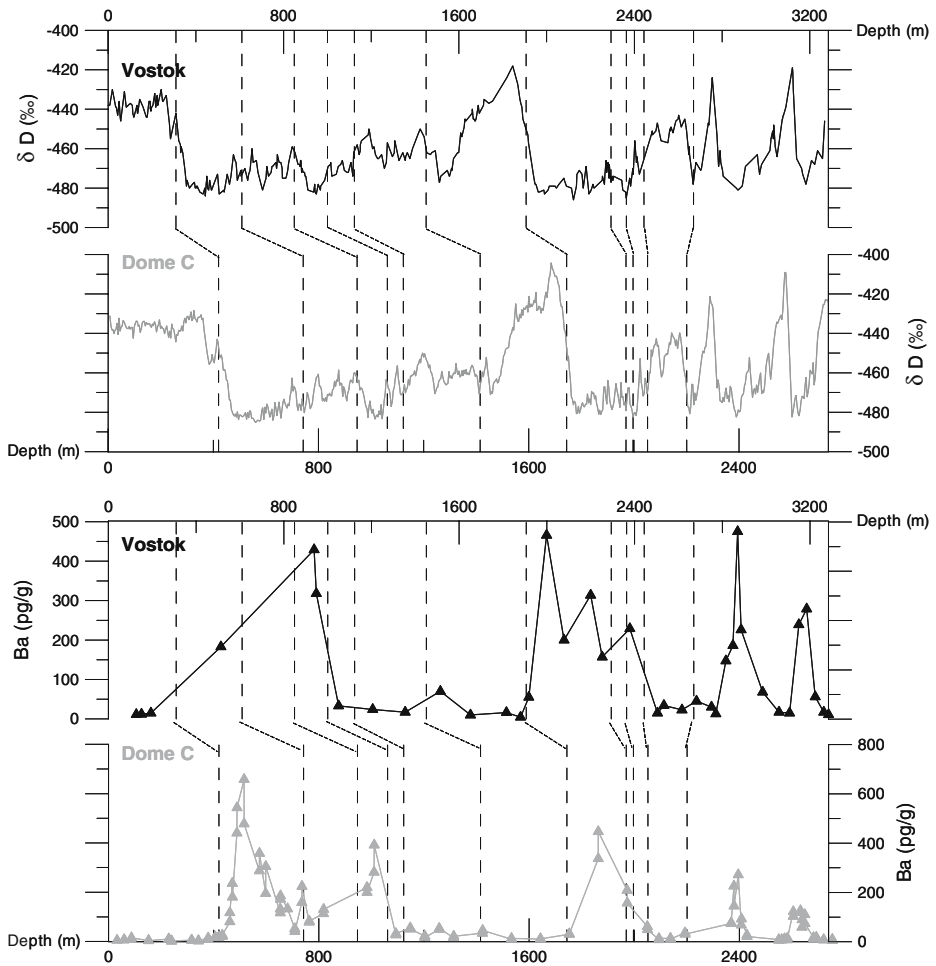


Fig. 4 Comparison of the Ba concentration profiles obtained at Dome C (this work and Gabrielli et al. 2005b) and Vostok (Gabrielli et al. 2005a) for the past 420 kyr. Also shown are the variations of the deuterium concentrations from EPICA community members (2004) and Petit et al. (1999). The vertical dotted lines correspond to 10 major dust events observed in both cores by Delmonte et al. (2004)

previously observed for insoluble dust (EPICA Community members 2004), giving support for these three elements being mainly derived from the continental dust.

The situation appears to be different for Cr. For this element, EF_c close to unity are observed during the coldest climatic stages, but moderately elevated values (up to 10) are observed during warmer periods, especially interglacial periods. Moreover, lower maximum/minimum element concentrations ratios are observed for this element (~ 50). It indicates that the atmospheric cycle of this element was dominated by crustal dust during the coldest climatic stages while contributions from additional sources were probably significant during warmer periods, especially interglacials. This may indicate changes in continental dust source areas or transport processes between glacial and interglacial periods (Röthlisberger et al. 2002; Delmonte et al.

2002; Gabrielli et al. 2005a, b; Wolff et al. 2006). It might also relate to the high relative contribution of volcanic emissions to the atmosphere during interglacial periods (Vallelonga et al. 2005).

3.4 Crustal trace elements versus climate relationship

As illustrated in Fig. 5 for Cr, Fe, Ba and dust, concentrations of crustal trace elements in Dome C ice from 263 to 672 kyr BP remain very low for δD values between $\sim -380\text{‰}$ and $\sim -430\text{‰}$, but shows a sharp increase for δD values below $\sim -430\text{‰}$. It suggests that there is a critical point in the climate mechanism, beyond which the physical and chemical processes of fallout and deposition of crustal elements to the Antarctic Plateau increase enormously. A possibility is that when a critical temperature gradient between low and high latitude was reached, it causes large changes in wind strength, then allowing larger amounts of crustal trace elements to be transported to the Antarctic ice cap (Gabrielli et al. 2005a). Another possibility could be rapid changes in local conditions in the different source areas such as Patagonia or Australia (Delmonte et al. 2002; Revel-Rolland et al. 2006).

3.5 The mid Brunhes climate shift

The mid Brunhes event (“MBE”) is a phase of global climatic change around 430 kyr, which was forced by the orbital eccentricity cycle (EPICA Community members

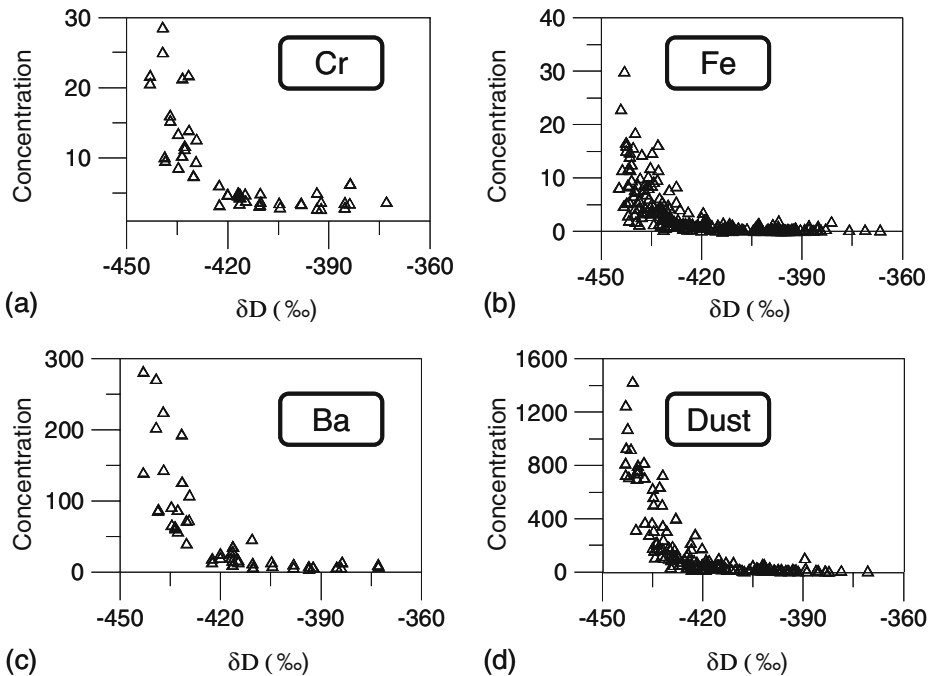


Fig. 5 EPICA/Dome C Antarctic ice core: changes in concentrations of Cr, Ba, Fe and Dust as a function of the deuterium content of the ice from 263 to 672 kyr BP. Concentrations in pg/g for Cr and Ba and in ng/g for Fe and Dust. Fe values from this work and Wolff et al. (2006)

2004). Terrestrial and marine geological temperature records indicate that before the MBE, the glacial cycles display smaller amplitudes (McManus 2004). Even if the coldest periods of the glacial portions of each climatic cycle are roughly similar before and after the MBE, the magnitude of the interglacial periods is clearly less pronounced (Jansen et al. 1986).

The fact that interglacial periods are less warm before the MBE does not seem to result in higher concentrations of the different crust derived elements during these pre-MBE interglacials, compared with those observed during post-MBE interglacials, as illustrated in Fig. 3.

The situation appears to be different for glacial maxima. High concentrations observed for the various elements (except Cr) during these glacial maxima appear to be lower before the MBE than after the MBE, despite the fact that δD values during these maxima are similar before and after the MBE (Fig. 3).

Figure 6 compares changes in Rb and Ba concentrations as a function of δD before and after the MBE, using a logarithmic scale for concentrations. It can be seen that the relation between concentrations and δD is very similar before and after the MBE.

After normalization using U concentrations, U, Rb and Ba concentrations measured in all our samples both for glacial maxima and interglacials periods are shown in Fig. 7 using ternary diagrams. Different symbols have been used for samples dated from before the MBE (which are shown using crosses) and the samples dated from after the MBE (which are shown using open triangles). It can be seen that during glacial maxima, the data points are very well grouped together both after and before the MBE (Fig. 7a), pointing toward a well defined crustal input. The situation appears to be different for interglacial periods, with rather dispersed data points (Fig. 7b), suggesting more complex and variable crustal inputs during these periods.

There are various possible explanations for these changes, which could be linked with changes in sources areas (Delmonte et al. 2004), atmospheric transport (Krinner and Genthon 2003) and strength of the Antarctic circumpolar vortex (Berger and Wefer 2003).

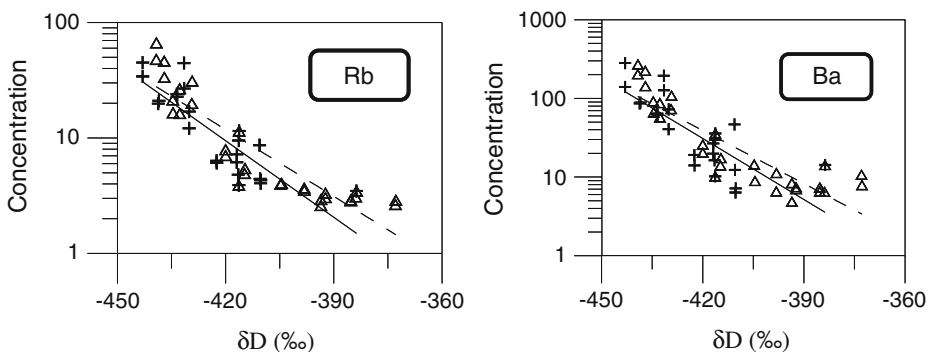


Fig. 6 EPICA/Dome C Antarctic ice core: changes in Rb and Ba concentrations (expressed in pg/g) as a function of the deuterium content of the ice before the Mid-Brunhes Event (MBE; crosses and continuous line) and after the MBE (open triangles and dotted line). A logarithmic scale is used for concentrations

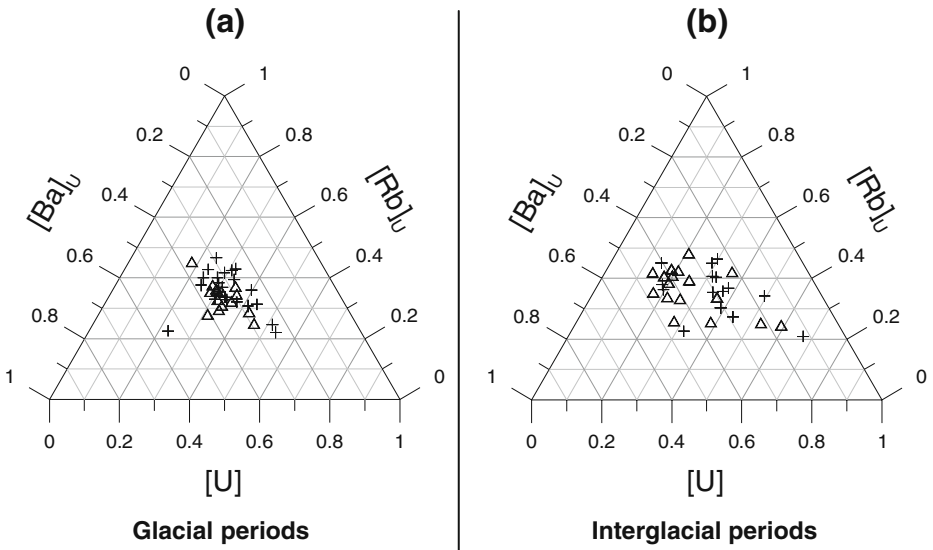


Fig. 7 EPICA/Dome C Antarctic ice core: ternary plots for U, Rb, and Ba (Rb and Ba concentrations have been normalized to U concentrations). **a** Glacial maxima from MIS 8.2 to MIS 16.2; **b** interglacial periods from MIS 9.3 to MIS 15.5. Crosses are used for ice dated from before the MBE, while open triangles are used for ice dated from after the MBE

3.6 Observed concentrations during the successive interglacials

As illustrated in Fig. 3, the data obtained in this work and in the work of Gabrielli et al. (2005b) include data for various interglacials from the Holocene (MIS1) to MIS 15.5 (~600 kyr BP). Amongst these interglacials are MIS 11 which is easily recognized in ice cores and other paleorecords as an exceptionally long interglacial (EPICA community members 2004), during which the Earth's orbital parameters were similar to present day ones (Berger and Loutre 2003). There are indications that every interglacial is probably different, with changing amplitude, duration and shape, as discussed by Wolff et al. (2007).

The only elements for which we have data for each of the seven interglacials considered in this work and the work of Gabrielli et al. (2005b) are Cr, Fe, Rb and Ba. Mean concentration values determined in the successive interglacials are given in Table 2.

Of particular interest is the comparison between concentration values observed during the Holocene, MIS 5.5, MIS 7.5, MIS 9.3 and MIS 11.3, Table 2. These five interglacials are indeed characterized by temperatures above Holocene temperatures. It can be seen that Cr and Rb concentrations are similar during these five interglacials, while Fe and Ba concentrations are more variable. For these last two elements, higher values are observed for interglacials 5.5, 7.5 and 9.3.

The highest values are observed during MIS 5.5 and 9.3, which are interglacials similar in shape, temperature and amplitude. For each of these two interglacials, there is a warm period followed by a relatively rapid cooling (Petit et al. 1999). This cooling resulted into an enhancement of dust emission in source areas because of an intensification of the wind strength in these areas and an enlargement/displacement

Table 2 Dome C, East Antarctica: mean concentrations of various crustal trace elements for the successive interglacial periods back to MIS 15.5

MIS number	1	5.5	7.5	9.3	11.3	13.3	15.1	15.5
Time period (kyr BP)	0.5–12	121–132	240–244	324–335	395–423	511–528	567–579	608–620
Number of samples	16	4	6	8	8	6	4	2
δD (‰) ^a	−396.1	−382.5	−388.9	−387.8	−391.2	−418.9	−402.0	−402.2
Cr	4.0	5.0	–	5.6	4.4	6.8	5.5	4.5
Fe	0.2	0.3	0.6	0.6	0.6	0.5	0.1	0.2
Rb	4.7	5.0	–	3.0	3.9	10.5	4.0	5.0
Ba	6.6	20.2	–	29.0	9.9	28.3	7.0	9.0

Concentrations are expressed in pg/g except for Fe (ng/g). Data for Cr, Rb and Ba for MIS 1 and 5.5 from Gabrielli et al. (2005b). Fe data for MIS 1 to 7.5 from Wolff et al. (2006)

^aEPICA community members (2004)

of the sources, then resulting into the high concentrations we observe during these two interglacials.

3.7 Observed concentrations during the successive glacial maxima

The data obtained in this work and in the work of Gabrielli et al. (2005b) include data for eight successive glacial maxima from MIS 2.2 (Last Glacial Maximum) to MIS 16.2. As illustrated in Fig. 3, it appears that the amplitude of these maxima probably shows a decreasing trend from MIS 2.2 to MIS 16.2. This is especially clear for Rb and Ba. For these two elements, the maxima observed for the most recent glacial maxima such as MIS 2.2 and 4.2 are indeed well pronounced, while the maxima are much less pronounced for the oldest glacial maxima such as MIS 14.2, 14.4 and 16.2.

One possible explanation for these changes in the amplitude of the maxima in concentrations could be linked with changes in the size distribution of dust particles transported from mid-latitude areas such as Patagonia to the Antarctic ice cap, with a decreasing trend in the dust size (as reflected by the fine particle percentage, which is defined as the proportion of particles with a diameter between 1 and 2 μm of the total dust mass, typically between 1 and 5 μm) over the last 500 kyr (Lambert et al. 2008), leading to a stronger aeolian deflation of Southern South America. This phenomenon could be combined with a significantly longer atmospheric particle lifetime in the upper troposphere due to a reduced hydrological cycle. Both arguments could explain the increase in the amplitude of the concentration maxima we observe in Dome C ice during the past 672 kyr.

4 Conclusion

This work has allowed documentation of large natural variations in the occurrence of several crust derived elements in Antarctic ice over the past 672 kyr. It will now be interesting to study other elements which mainly derive from crustal dust, especially Rare Earth Elements. It will be also of interest to extend this study to preceding climatic cycles which are covered in the bottom part of the EPICA Dome C ice core back to MIS 20.2, \sim 800 kyr BP.

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Appendix A

Table 3 EPICA/Dome C Antarctic ice core: Cr, Fe, Rb, Ba and U concentrations measured in ice from 78 depth intervals from 2368.85 to 3062.13 m

Depth (m)	Age (kyr BP)	Concentration									
		Cr	±	Fe	±	Rb	±	Ba	±	U	±
2,368.85	263.6	9	1.7	1	0.06	21	1	73	3	0.2	0.01
2,369.12	263.7	9	1	1	0.03	19	1	76	3	0.4	0.07
2,379.85	267.5	16	1	17	0.3	46	1	225	3	1.2	0.1
2,380.13	267.6	15	3	12	0.3	34	1	144	4	0.9	0.2
2,396.35	274.3	25	2	28	0.6	67	2	271	5	1.3	0.2
2,396.63	274.4	29	4	22	0.4	48	2	204	3	1.7	0.5
2,407.35	278.8	9	0.8	4	0.1	17	1	67	1	0.3	0.07
2,407.63	278.9	13	3	6	0.1	21	2	92	2	0.4	0.1
2,429.35	286.4	5	0.9	0.8	0.05	7	0.4	26	2	< 0.1	0.05
2,429.63	286.5	5	0.8	1.1	0.09	8	0.3	20	1	0.1	0.02
2,550.35	327.4	5	0.7	0.6	0.02	3	0.1	8	0.4	0.02	0.004
2,550.63	327.5	3	0.5	0.2	0.03	3	0.1	5	0.2	< 0.02	0.01
2,561.35	330.1	3	0.5	0.3	0.04	3	0.2	7	0.3	0.03	0.006
2,561.63	330.1	4	0.5	0.3	0.1	3	0.2	7	0.2	0.02	0.004
2,572.35	332.7	16	3	0.3	0.08	3	0.2	8	0.9	< 0.02	0.01
2,572.63	332.7	4	0.4	1	0.1	3	0.1	11	0.7	0.07	0.008
2,583.35	334.8	4	0.6	0.2	0.01	3	0.3	7	0.1	< 0.02	0.01
2,583.63	334.8	6	1.3	1	0.03	3	0.3	14	0.3	0.05	0.01
2,605.35	343.4	10	2	2	0.1	26	3	121	6	0.6	0.1
2,605.63	343.6	13	2	3	0.1	25	2	102	4	0.5	0.1
2,632.85	358.9	12	1	3	0.1	25	1	125	5	1.1	0.2
2,633.13	359.1	12	1	2	0.1	22	1	118	2	0.6	0.04
2,638.35	362.2	12	2	4	0.4	16	1	58	3	0.4	0.09
2,638.63	362.3	11	2	5	0.4	27	1	88	2	0.6	0.1
2,649.35	368.3	13	4	7	1	31	1	109	8	1.1	0.2
2,649.63	368.5	9	2.8	4	0.7	20	1	73	3	0.4	0.05
2,682.35	385.9	4	0.8	0.4	0.05	5	0.3	16	0.4	0.06	0.02
2,682.63	386.1	4	0.6	0.3	0.01	4	0.2	10	0.3	0.03	0.01
2,693.35	391.9	4	0.8	0.6	0.06	5	0.4	17	0.3	0.05	0.01
2,693.63	392.1	5	0.6	0.8	0.03	5	0.4	14	0.4	0.04	0.01
2,720.85	402.7	4	0.5	0.3	0.01	3	0.1	7	0.1	< 0.05	0.02

Table 3 (continued)

Depth (m)	Age (kyr BP)	Concentration									
		Cr	±	Fe	±	Rb	±	Ba	±	U	±
2,721.13	402.8	3	0.8	0.2	0.03	3	0.1	7	0.3	< 0.05	0.03
2,753.85	414.4	6	0.9	0.1	0.01	3	0.1	4	0.1	< 0.04	0.02
2,754.13	414.5	8	0.3	0.1	0.01	4	0.3	9	0.3	0.13	0.03
2,764.85	419.4	4	0.6	0.3	0.03	4	0.4	7	0.2	0.15	0.02
2,765.13	419.5	3	0.7	0.3	0.07	4	0.2	11	0.2	< 0.02	0.01
2,775.85	425.0	4	0.4	0.5	0.05	4	0.3	14	0.4	0.03	0.005
2,776.13	425.2	3	0.6	0.3	0.03	4	0.5	9	0.3	< 0.03	0.01
2,786.85	432.9	22	4	21	1	45	2	282	6	1.2	0.3
2,787.13	433.1	21	4	14	0.5	34	2	140	3	0.7	0.2
2,803.35	449.7	14	2	11	0.3	27	1	127	1	0.6	0.1
2,803.63	450.0	22	2	20	0.3	45	2	194	8	0.7	0.2
2,808.85	455.6	10	2	2	0.2	30	3	112	3	0.6	0.1
2,809.13	455.9	27	2	7	0.2	25	2	261	6	0.6	0.1
2,825.35	474.6	8	1.3	1	0.1	12	1	57	2	0.7	0.2
2,825.63	474.9	9	0.6	1	0.1	10	1	42	2	0.5	0.09
2,830.85	479.6	4	0.6	2	0.2	12	1	36	1	0.2	0.04
2,831.13	479.9	5	0.8	1	0.04	10	1	30	2	0.2	0.04
2,847.35	491.8	5	0.9	0.2	0.02	4	0.3	6	0.1	0.04	0.01
2,847.63	492.0	4	0.8	0.3	0.04	4	0.4	7	0.3	0.05	0.01
2,874.85	511.3	3	0.5	0.6	0.07	6	0.5	14	1	0.03	0.01
2,875.13	511.5	6	0.9	0.7	0.02	6	0.4	19	1	< 0.05	0.02
2,902.35	528.4	8	1	0.3	0.07	15	1	40	2	0.3	0.04
2,902.63	528.6	9	1	0.4	0.07	15	1	40	1	0.3	0.04
2,907.85	532.8	8	0.9	7	0.2	17	1	72	3	0.4	0.1
2,908.13	533.1	7	1	5	0.2	12	1	41	2	0.2	0.05
2,913.35	538.2	21	4	8	0.5	23	1	62	4	0.4	0.1
2,913.63	538.5	10	0.6	8	0.1	24	1	64	4	0.3	0.1
2,929.85	554.3	5	0.6	0.8	0.07	6	0.4	20	1	0.08	0.01
2,930.13	554.4	5	0.6	1.3	0.07	7	0.2	27	2	0.1	0.04
2,946.35	562.8	6	0.7	0.1	0.07	4	0.2	11	0.8	0.1	0.04
2,946.63	562.9	3	0.4	–	–	4	0.2	6	0.6	< 0.2	0.1
2,957.35	566.7	5	0.5	–	–	4	0.1	5	0.3	0.09	0.02
2,957.63	566.8	4	0.2	–	–	3	0.1	4	0.2	0.03	0.01
2,979.35	574.4	10	1	0.2	0.01	5	0.2	10	0.1	0.08	0.02
2,979.63	574.5	3	0.2	0.1	0.01	4	0.2	9	0.5	0.06	0.01
3,006.85	591.3	8	0.3	0.7	0.03	17	1	43	1	0.3	0.1
3,007.13	591.6	8	0.3	0.8	0.04	19	1	55	2	0.5	0.1
3,017.85	604.2	3	0.6	0.5	0.04	4	0.2	12	1	0.03	0.01
3,018.13	604.5	3	0.4	1.0	0.09	9	0.4	47	2	0.2	0.06
3,028.85	616.3	6	0.4	0.1	0.02	5	0.1	9	0.3	0.08	0.01
3,029.13	616.6	3	0.5	0.3	0.03	5	0.2	9	0.6	0.06	0.02
3,039.85	632.0	10	1	8	0.2	20	1	86	4	0.5	0.1
3,040.13	632.6	10	1	8	0.4	21	1	88	2	0.5	0.1
3,050.85	655.6	8	0.6	2	0.03	22	1	80	1	0.4	0.1
3,051.13	656.1	7	0.7	1	0.04	18	1	62	3	0.6	0.1
3,061.85	671.7	10	1	2	0.06	28	2	109	6	0.9	0.2
3,062.13	672.0	10	1	2	0.1	25	1	102	4	0.7	0.1

The length of each sample is about 20 cm (see Section 2.2), and the depth given in the table is the depth for the top of the sample. The age of the ice is from the EDC3Beta6 timescale from Parrenin et al. (2007). Concentrations are expressed in pg/g, except for Fe (ng/g). Uncertainties are 95% confidence intervals

Appendix B

Table 4 EPICA/Dome C Antarctic ice core: crustal enrichment factor (EFc) for Cr, Fe, Rb and U in ice from 78 depth intervals, using Ba as crustal reference element

Depth (m)	Age (kyr BP)	EFc			
		Cr	Fe	Rb	U
2,368.85	263.6	2.4	0.4	1.8	0.6
2,369.125	263.7	2.2	0.3	1.5	1.3
2,379.85	267.5	1.4	1.6	1.2	1.3
2,380.13	267.6	2	1.9	1.4	1.7
2,396.35	274.3	1.8	2.3	1.5	1.2
2,396.63	274.4	2.7	2.3	1.4	2.3
2,407.35	278.8	2.5	1.4	1.5	1.1
2,407.63	278.9	2.8	1.4	1.4	1.3
2,429.35	286.4	3.5	0.7	1.6	1
2,429.63	286.5	4.5	1.2	2.3	1.3
2,550.35	327.4	11.5	1.5	2.1	0.6
2,550.63	327.5	11	0.7	3.2	1
2,561.35	330.1	7.1	0.9	2.7	1
2,561.63	330.1	10.1	1	2.6	0.7
2,572.35	332.7	39.5	0.9	2.2	0.5
2,572.63	332.7	6.7	2.7	1.5	1.8
2,583.35	334.8	10.3	0.7	2.9	0.7
2,583.63	334.8	8.5	1.8	1.5	0.8
2,605.35	343.4	1.6	0.3	1.3	1.4
2,605.63	343.6	2.4	0.6	1.5	1.3
2,632.85	358.9	1.8	0.6	1.2	2.3
2,633.13	359.1	2	0.3	1.1	1.4
2,638.35	362.2	3.9	1.6	1.7	1.7
2,638.63	362.3	2.5	1.3	1.8	1.8
2,649.35	368.3	2.2	1.4	1.7	2.5
2,649.63	368.5	2.5	1.2	1.6	1.3
2,682.35	385.9	4.1	0.5	1.8	0.9
2,682.63	386.1	8.3	0.6	2.3	0.7
2,693.35	391.9	4.3	0.8	1.9	0.7
2,693.63	392.1	6.6	1.2	2.1	0.8
2,720.85	402.7	10.5	1.1	2.6	1.9
2,721.13	402.8	7.7	0.7	2.4	2
2,753.85	414.4	33.4	0.4	5.8	3
2,754.13	414.5	18.5	0.3	3	4.1
2,764.85	419.4	10.3	0.8	3.4	6.1
2,765.13	419.5	5.8	0.6	1.9	0.6
2,775.85	425.0	4.7	0.7	1.7	0.5
2,776.13	425.2	6.4	0.7	2.7	0.9
2,786.85	432.9	1.5	1.6	1	1.1
2,787.13	433.1	2.8	2.2	1.5	1.3
2,803.35	449.7	2.1	1.8	1.3	1.2

Table 4 (continued)

Depth (m)	Age (kyr BP)	EFc			
		Cr	Fe	Rb	U
2,803.63	450.0	2.1	2.2	1.4	1
2,808.85	455.6	1.7	0.4	1.6	1.4
2,809.13	455.9	2	0.6	0.6	0.6
2,825.35	474.6	2.7	0.5	1.3	3.5
2,825.63	474.9	4.1	0.5	1.4	3
2,830.85	479.6	2.4	1	2	1.3
2,831.13	479.9	3.2	0.9	2	1.5
2,847.35	491.8	14.9	0.7	3.9	1.5
2,847.63	492.0	10	1	3.6	1.7
2,874.85	511.3	4.5	0.9	2.6	0.6
2,875.13	511.5	6.1	0.8	2	0.7
2,902.35	528.4	3.6	0.1	2.3	1.9
2,902.63	528.6	4.3	0.2	2.3	2.3
2,907.85	532.8	2	2.1	1.4	1.4
2,908.13	533.1	3.5	2.8	1.8	1.3
2,913.35	538.2	6.6	2.7	2.2	1.5
2,913.63	538.5	3.1	2.8	2.3	1.4
2,929.85	554.3	4.5	0.8	1.9	1.1
2,930.13	554.4	3.6	1.1	1.6	1.1
2,946.35	562.8	–	0.2	2.4	3.6
2,946.63	562.9	–	0.1	3.9	9.1
2,957.35	566.7	17.7	0.1	4.8	5
2,957.63	566.8	18	0.1	4.9	2.3
2,979.35	574.4	17.9	0.4	2.9	2
2,979.63	574.5	7.1	0.1	2.8	2
3,006.85	591.3	3.6	0.3	2.3	2.1
3,007.13	591.6	2.8	0.3	2	2.5
3,017.85	604.2	5.2	0.8	2.2	0.6
3,018.13	604.5	1.3	0.4	1.1	1
3,028.85	616.3	13.4	0.3	3.6	2.3
3,029.13	616.6	7.1	0.6	3.3	1.9
3,039.85	632.0	2.2	2	1.4	1.5
3,040.13	632.6	2.1	2	1.4	1.6
3,050.85	655.6	2.1	0.2	1.8	2.7
3,051.13	656.1	1.9	0.4	1.7	1.2
3,061.85	671.7	1.8	0.4	1.6	2.1
3,062.13	672.0	1.9	0.5	1.5	1.9

The length of each sample is about 20 cm (see Section 2.2), and the depth given in the table is the depth for the top of the sample. The age of the ice is from the EDC3Beta6 timescale from Parrenin et al. (2007)

Appendix C

Study of the influence of the dust content of the water used for the preparation of the standards used for the calibration of the Element2 ICP-SFMS instrument.

Synthetic matrix: standards prepared from 1,000 ppm certified solutions by dilution using ultra-pure water produced in the laboratory. Interglacial matrix: standards prepared from 1,000 ppm certified solutions by dilution using melted Dome C ice dated from interglacial period (low dust content). Glacial matrix: standards prepared from 1000 ppm certified solutions by dilution using melted Dome C ice dated from glacial maxima (high dust content). The values given in the table are the slope of the linear calibration curve (intensity of the ICP-SFMS signal expressed in counts per seconds versus concentration of the different elements in the different standards). Cr, Fe, Rb, Ba and U concentrations in the standards were chosen so that they overlap concentrations observed in Dome C Antarctic ice. No significant difference in the slope of the calibration curve is observed for the different matrices for Cr, Rb and Ba. Significant differences are observed for Fe both for interglacial and glacial maxima matrices, and U for interglacial matrices.

Firstly some glacial and interglacial EPICA/Dome C ice samples (inner core) were analysed by ICP-SFMS. Cr, Fe, Rb, Ba and U concentrations in these samples are illustrated in Table 5.

Taking into consideration the levels of these elements in glacial and interglacial EPICA/Dome C ice samples, different sets of multi-element standard solutions were prepared: one set of “synthetic” matrix, one set of “glacial” matrix, one set of “interglacial” matrix. The concentration in the final standard solutions ranged from 0 to 200 pg g^{-1} . The elements of the different matrices standard solution were determined by ICP-SFMS with a nebulisation/desolvation introduction system and without (Table 6, Slope). The slope of the regression line for each trace element, expressed in count per seconds per pg g^{-1} , was calculated for each matrix, with and without the use of the Aridus during the measurements, as illustrated in Table 6, Effect.

Because of a very high enhancing effect of glacial and interglacial matrix on trace elements signals with the use of Aridus (>5%), it was decided to do the analysis of trace elements on which this thesis is based with a micro-flow (<100 $\mu\text{l min}^{-1}$) PFA nebulisation system and not with the Aridus system.

The only two elements for which significant effects were observed are Fe (up to 60%) whatever the period and U during interglacial times (up to 16%; see Table 6). It shows that when using standards prepared with laboratory ultra-pure water, U concentrations are under-estimated for interglacial periods while Fe concentration are overestimated whatever the period. A systematic correction was then applied for these two elements.

Table 5 Average concentrations in glacial maxima ice sample ($n = 34$) and interglacial ice samples ($n = 44$) of the EPICA Dome C ice core by ICP-SFMS

Element	Average concentration during glacial maxima (pg g^{-1})	Average concentration during interglacials (pg g^{-1})
Cr	13	5
Fe ^a	7.4	0.5
Rb	26	6
Ba	114	17
U	0.6	0.12

^aConcentration expressed in ng g^{-1}

Table 6 Slope of the regression line for each trace element for various matrices and the effect of matrix on trace elements signals

Element	Slope						Effect			
	Without Aridus			With Aridus			Element			
	Synthetic matrix	Interglacial matrix	Glacial matrix	Synthetic matrix	Interglacial matrix	Glacial matrix	Without Aridus	With Aridus	With Aridus	
							$((IG - S)/S) \times 100$	$((IG - S)/S) \times 100$	$((IG - S)/S) \times 100$	
Cr	9.6	9.4	9.4	95	110	138	Cr	-2.5	-1.9	16.4
Fe	11.4	16.2	18.2	84	104	176	Fe	42.8	60.3	109.7
Rb	321	316	321	1,377	1,665	2,043	Rb	-1.6	0.3	48.3
Ba	275	275	272	1,344	1,667	2,024	Ba	0.1	-1.0	50.6
U	37	31	39	2,211	2,845	3,456	U	-16.4	4.5	28.7

Negative values represent an under-estimation compared to the real values whilst positive values represent an over-estimation compared to the real values. Bold letters show a high enhancing effect of the matrix on trace element signal
IG Interglacial matrix, *G* glacial matrix, *S* synthetic matrix

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