

# A two century record of strontium isotopes from an ice core drilled at Mt Blanc, France

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## Abstract

New techniques which allow small amounts of Sr to be reliably analysed [G.R. Burton, V.I. Morgan, C.F. Boutron, K.J.R. Rosman, High-sensitivity measurements of strontium isotopes in polar ice, *Anal. Chim. Acta* 469 (2002) 225–233] by TIMS (Thermal Ionisation Mass Spectrometry) have been used to measure the isotopic composition of Sr and the concentration of Rb and Sr at sub-nanogram per gram levels in a Mt Blanc snow and ice core. This two century time series of Sr isotopes is the first to be reported in an Alpine glacier. The Sr and Rb concentrations range from 3 ng/g to 20 pg/g and 1 ng/g to 10 pg/g, respectively, with higher concentrations evident in more recent times. This trend is consistent with that reported previously for other metals such as Cd, Cu and Zn [K. Van de Velde, C. Barbante, G. Cozzi, I. Moret, T. Bellomi, C. Ferrari, C. Boutron, Changes in the occurrence of silver, gold, platinum, palladium and rhodium in Mont Blanc ice and snow since the 18th century, *Atmos. Environ.* 34 (2000) 3117–3127; K. Van de Velde, C. Boutron, C. Ferrari, T. Bellomi, C. Barbante, S. Rudnev, M. Bolshov, Seasonal variations of heavy metals in the 1960s Alpine ice: sources versus meteorological factors, *Earth Planet. Sci. Lett.* 164 (1998) 521–533; K.J.R. Rosman, C. Ly, K. Van de Velde, C.F. Boutron, A two century record of lead isotopes in high altitude Alpine snow and ice, *Earth Planet. Sci. Lett.* 176 (2000) 413–424]. The <sup>87</sup>Sr/<sup>86</sup>Sr ratios vary between 0.7020 and 0.7176 and display relatively larger variations in recent times which have been attributed to seasonal variations made evident by the increased sampling resolution available at shallower depths. No change with time is evident in this ratio which has a mean value of ~0.712 and is similar to Glacial ice at Summit Greenland, suggesting that aerosols reaching Mt Blanc represent the same mixture of sources. Also, anthropogenic sources would appear to have the same isotopic ratio. The presence of Saharan dust in some samples is confirmed here by their strontium isotopic ratios.

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## 1. Introduction

For over 60 yr Sr isotopes have been measured for the purposes of geochronology and isotope geochemis-

try [5]. In recent times there has been increasing interest in Sr as an isotopic tracer in environmental studies. There is the potential to characterise dust inputs at a certain site by transport of material from source areas if the isotopic compositions of the site and source areas are known. Furthermore, sources and transport mechanisms may elucidate previous climatic conditions. For

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instance, Sr and Pb isotopes have been used to determine the sources of particulate and dissolved matter in a river in flood [6] while Sr isotope systematics allowed the origin of groundwaters from granitoids in France to be deciphered [7]. Sr together with Nd isotopic ratios have been used to show that continental dust deposited in ice at Vostok and Dome C sites in East Antarctica during the colder glacial stages is of Patagonian origin [8,9]. Also, the probable origin of dust deposited at Summit, Greenland, in 23–26 ky ice was found to be east Asia [10].

Very little trace metal, isotopic, time-series data are available in the literature. Even less data extend beyond a few years in very recent times or are more than a small number of sparse data points within the last two glacial cycles. Most of the data available come from polar locations. To our knowledge, our measurement of Sr isotopes from Mt Blanc, a continental glacier, extending over the last 200 yr is unique.

This is the first Sr isotope time series measured at sufficient resolution to demonstrate the existence of seasonal Sr isotope variations earlier than very recent times. This is important because often we must rely on older archives for the retrieval of seasonal data. Prehistoric ice core samples generally integrate many years of snow deposition and this means that the individual aerosol components archived in the ice are averaged out in the sample. A high-resolution study has the potential to retrieve these aerosol components and define their source. This information may prove useful when interpreting prehistoric events.

The sample location has the advantage of possibly combining local and long range inputs with each contributing natural and anthropogenic components. This may allow us to study the relationship between the sources of aerosols and weather patterns, both local and global.

## 2. Experimental procedures

### 2.1. Sampling

The 10 cm diameter Mt Blanc snow and ice core was drilled to a depth of ~140 m in June 1994 at Dome du Gouter at an elevation of 4.3 km and approximately 1.5 km north-west of Mt Blanc in south-east France [11]. The site receives a mean annual snow accumulation rate of  $3.5 \text{ m yr}^{-1}$ , the mean annual temperature is  $-11 \text{ }^\circ\text{C}$  and the close-off depth is ~60 m. An electromechanical drill coated with Teflon (PTFE) was used to limit contamination. The top of the core corresponds to ~1991 AD and the bottom to ~200 yr

BP. Dating was achieved by using an ice flow model coupled with  $^{210}\text{Pb}$  (natural) and  $^{137}\text{Cs}$  (thermonuclear fallout in 1963 at 90 m and Chernobyl in 1986 at 39 m) activity markers [11]. The depth–age scale is not linear. Annual layers become thinner with depth. Typically, an annual layer at the surface was ~7 m thick while 2 m thick at 50 m depth and 1 m thick at 100 m. A tentative depth–age scale was constructed by interpolation for depths greater than 110 m, assuming that the ice at 136 m was 200 yr old. These are the ages shown in Table 2. The dating accuracy was estimated to be ~1 yr from the surface to 1960, ~5 yr at 1940 and 50 yr at 1800. Seasonal variation in trace metal concentrations could not be used to systematically date the core because only parts of the core were available for this project.  $\delta\text{D}$  (deuterium) was measured on all sections analysed but it was only used to distinguish summer and winter samples [4].

### 2.2. Samples

Fifty six samples from 27 core sections, taken at various depths (see Table 2), were analysed. Each section consisted of top, middle and bottom parts. Between sections, ~2.5 cm of contaminated ice was removed, giving sampling gaps of ~2 weeks [4]. For 16 of the sections, aliquots of the parts were pooled prior to analysis in an attempt to utilise resources efficiently. The individual parts were measured for the other 11 sections. Two lengths of the core, 81.4–83.7 m (Sections 96, 97 and 98) spanning winter 1967/68 to winter 1966/67 and 92.8–94.4 m (Sections 111 and 112) spanning summer 1961 to summer 1960 were sampled continuously to investigate seasonal variations.

Each core section was decontaminated at the LGGE using the procedures described by Candelone et al. [12]. After mechanically removing the outer material in concentric layers, the central inner core was melted and aliquots were prepared in acid cleaned LDPE bottles, then frozen. The frozen aliquots of each sample were transported to Curtin University in Perth, Western Australia, where the Rb and Sr isotopes were measured. The efficacy of the decontamination process was investigated [3,2] by analysing the concentric layers and it was concluded that contamination had not penetrated the central inner core.

### 2.3. Sample preparation

Samples were processed following the technique described by Burton et al. [1]. Sample processing was carried out in a laboratory supplied with HEPA-filtered

air using ultra-pure acids, and pre-cleaned PFA beakers. The samples, together with 100  $\mu\text{L}$  ultra-pure concentrated HF and 10  $\mu\text{L}$  ultra-pure concentrated  $\text{HNO}_3$  were spiked with  $^{84}\text{Sr}$  (SRM 988, National Institute of Science and Technology, USA) and  $^{85}\text{Rb}$  (Oak Ridge National Laboratory, USA) to allow the Sr isotopic composition and concentration to be determined in a single measurement by IDMS. Addition of  $^{85}\text{Rb}$  allowed the Rb concentration to be determined by IDMS on the same sample aliquot but in a separate measurement. The spiked samples were then evaporated slowly ( $\sim 3$  h) to dryness on a hotplate with heat lamps overhead.

The sample residue was re-dissolved and transferred to microliter-scale Sr-Spec resin (Eichrom Industries, Illinois, USA) ion-exchange columns where procedures described by Burton were followed. The eluted samples were evaporated to dryness.

No attempt has been made to separate the marine or detrital components of the samples. If it is assumed the samples are a mixture of crustal or shale like materials (Na/Al ratios between 0.36 [13] and 0.11 [14], respectively) and seawater (Na/Al ratio =  $3.6 \times 10^7$  [15]) then according to the Na/Al data [3] seawater contributes less than 1 ppm of the total input. Therefore, using the average Sr concentration in the crust (350 ppb [13]) and seawater (7.8 ppm [15]) it is possible to estimate that the contribution of Sr due to seawater is less than 10 ppm. Such a small Sr contribution will have a negligible impact on the sample isotopic ratios.

To further confirm the negligible impact of marine Sr, we have conducted a detailed physical separation experiment on two of the samples by centrifuging and washing with ultra-pure water in an attempt to separate the soluble and insoluble components (see Table 1). These samples were chosen because they were both believed to contain Saharan dust, #1319 by van de Velde et al. [16] and #2030 by the authors (this work). Approximately 4 ml of each melted ice core sample was centrifuged in a pre-cleaned polyethylene tube for 10 min. The top 3 ml of solution, the “wash” was carefully removed by pipetting and stored. Approximately 3 ml of quartz-distilled ultra-pure water was added to the centrifuge tube and mixed. The mixture was centrifuged and this process was repeated twice more resulting in an aggregated “wash” and a “remainder” for each sample. If the sample does indeed contain soluble and insoluble fractions then we assume the soluble material is to be found in the “wash” and the insoluble in the “remainder”. The four sample separates, along with two procedural blank separates, were processed for mass spectrometry as described above.

Table 1  
Rb/Sr ratio and Sr isotopic composition of sample components

Section	ID	Year <sup>a</sup>	Depth <sup>b</sup>	Type <sup>c</sup>	Rb/Sr	$^{87}\text{Sr}/^{86}\text{Sr}$
57	1319	1981.1	54.1	Wash	0.28	$0.715 \pm 0.001$
				Remainder	0.39	$0.719 \pm 0.001$
111	2030	1960.7	93.6	Wash	0.21	$0.713 \pm 0.002$
				Remainder	1.21	$0.717 \pm 0.004$

Uncertainties are 95% confidence intervals.

<sup>a</sup> See text for discussion of dating. Decimal estimates of the dates are given assuming the snow accumulation to be constant within each section, using  $\delta\text{D}$  to identify winter/summer periods.

<sup>b</sup> The inner part of each core section (column #1) was broken into 0.1–0.4 m length subsections. The depth given is the upper extent of each section or subsection.

<sup>c</sup> “Wash” is assumed to contain soluble sample component, “remainder” is assumed to contain insoluble sample component. See text for discussion of sample processing.

There may be some value in selecting common grain size fractions from the samples in order to possibly separate long range, fine particles from short range, large ones, but this is not feasible here given the small sample quantities and the potential of contamination in carrying out the process. The approach also has the advantage that the character of inputs to Mt Blanc are preserved even though the interpretation may become more complex.

#### 2.4. Mass spectrometry

The mass spectrometry has been described in detail by Burton et al. [1] and will only be briefly described here. A VG354 isotope ratio mass spectrometer (Micromass, UK) was used for all measurements. This instrument has a  $90^\circ$  magnetic sector field and is fitted with a 16 sample turret, thermal ion source, 9 Faraday collectors and a Daly collector that is operated in analogue mode. Apart from extensive automatic degassing of the samples prior to analysis, they were analysed manually with the operator having full control over ion beam focussing and filament temperature. The relative efficiencies of the Faraday collectors used in the measurements were determined by switching Sr isotope ion beams between sets of collectors.

Sr samples were loaded onto degassed, tungsten filaments with  $\sim 3$   $\mu\text{L}$  of activator solution [17]. The filament temperature was increased to  $\sim 1000$   $^\circ\text{C}$  over  $\sim 5$  min. At this point the Rb isotopic composition in the Sr sample was measured with the Daly detector to allow a small and usually negligible correction to be made for the interference of  $^{87}\text{Rb}$  with  $^{87}\text{Sr}$ . The Rb present is due to a mixture of chemical and filament blanks and the

$^{85}\text{Rb}$  spike. The filament temperature was then increased to  $\sim 1350\text{ }^\circ\text{C}$  at which time the Sr isotope composition was measured including  $^{85}\text{Rb}$ . Measurements were made with the multi-collector when  $^{88}\text{Sr}$  ion currents of  $\sim 5 \times 10^{-12}\text{ A}$  were achieved. For smaller beams the Daly detector was used. This generally occurred with samples of less than  $\sim 500\text{ pg}$ , filament blanks ( $\sim 2\text{ pg}$ ) and procedural blanks ( $\sim 10\text{ pg}$ ).

Rb samples were loaded onto degassed, tantalum filaments with dilute  $\text{H}_3\text{PO}_4$ . The filament temperature was increased to  $\sim 1000\text{ }^\circ\text{C}$  over  $\sim 5\text{ min}$  at which time a Rb signal was usually observed. The signal was then increased to provide  $^{85}\text{Rb}$  ion currents of  $\sim 2 \times 10^{-13}\text{ A}$  on the Daly collector. Generally the samples yield less than  $\sim 500\text{ pg}$  of Rb.

NIST SRM 987 and Johnson-Matthey Specpure (JMSP)  $\text{SrCO}_3$  were used to monitor the accuracy and precision of the analyses. Thirteen analyses of SRM 987 yielded an  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.71027 \pm 0.00002$  (95%CI) which is the same within experimental uncertainty as our JMSP  $\text{SrCO}_3$  ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.71028 \pm 0.00002$ ,  $n = 10$ ). A quality control sample consisting of  $\sim 1\text{ ng}$  natural Sr (JMSP) and  $\sim 30\text{ pg}$   $^{84}\text{Sr}$  spike [1] was synthesised to assess the precision of the Sr ratios achieved after the measurement and deconvolution process. This solution was loaded on a filament in the same way as a sample. Repeated analysis yielded a Sr concentration of  $967.3 \pm 0.2\text{ pg g}^{-1}$  and  $^{87}\text{Sr}/^{86}\text{Sr} = 0.71036 \pm 0.00006$ ,  $n = 36$ , 95%CI.

Raw mass spectrometer data was output to a computer file as a set of 60 or more sets of ratios referenced to the  $^{86}\text{Sr}$  isotope (i.e.,  $^{84}\text{Sr}/^{86}\text{Sr}$ ,  $^{85}\text{Rb}/^{86}\text{Sr}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{88}\text{Sr}/^{86}\text{Sr}$ ). Since the spectrum fractionated during the analysis the ratios for each spectral scan were individually normalised to a common reference ratio before the final average was taken, in order to more correctly reflect the “in-run” precision. The standard error was then determined for each set of ratios and values outside 3 standard errors were rejected as outliers.

Knowledge of the  $^{84}\text{Sr}$  spike isotope composition coupled with non-variation of the  $^{84}\text{Sr}$ ,  $^{86}\text{Sr}$  and  $^{88}\text{Sr}$  isotope abundances in nature allows an algebraic deconvolution of the spike and unknown sample spectra. Isotopic fractionation of the spectrum is corrected by normalisation to  $^{88}\text{Sr}/^{86}\text{Sr} = 0.1194$  as part of the process. Both the Sr concentration and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic composition were determined in the same analysis.

Uncertainties were propagated through all calculations using a Monte-Carlo procedure [1] The final uncertainties were expressed as 95% confidence intervals.

### 3. Results and discussion

#### 3.1. Sample separation experiment

Table 1 shows the results of the physical separation experiment described in Section 2.3. The “wash” of both samples, are unlike seawater. Their Rb/Sr ratios, 0.28 and 0.21 respectively, are more like crustal material (Rb/Sr = 0.32 [13]) than seawater (Rb/Sr = 0.015 [15]). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the sample washes, 0.715 and 0.713, respectively, are also unlike seawater ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7091$  [18]) and rather more like the isotopic composition expected for Saharan dust ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.713\text{--}0.726$  [19]). The “remainders” of both samples have Rb/Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios different to their washes indicating that some separation of components has occurred. However, it is clear that physically separating components in the sample has more of an effect than simply removing the “marine imprint” because the “washes” do not have the expected marine Rb/Sr or  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Although the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the wash and remainder of sample 2030 do not differ significantly, they are both different to the marine signature. While the accuracy has deteriorated, as expected, we believe the results support the approach we have taken in this study. Namely, we make no attempt to physically or chemically separate the sample into fractions.

#### 3.2. Two century time series

Table 2 shows measurements of Rb and Sr concentrations and Sr isotopes in 56 samples of snow and ice dating from  $\sim 1991\text{ AD}$  to  $\sim 200\text{ BP}$ . The sample sections are divided into a top, middle and bottom part, providing extra resolution within the section. However, each section is widely spaced from the next section, ranging from 16 m at the top of the core to 5 m at the bottom. If all the measured data were plotted, we would see widely separated groups of high resolution data. Pooled or averaged data for each section provides a less distracting view of the data. The results of pooling either the sample aliquots prior to analysis, or the sample measurements after analysis by calculation (see Fig. 1 caption) are plotted in Fig. 1. Strontium and Rb concentrations range from 3 ng/g to 20 pg/g and 1 ng/g to 10 pg/g, respectively. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios vary between 0.7020 and 0.7176 with uncertainties of typically 0.0003 (but larger for smaller samples) allowing resolution of these differences.

A larger variation in Sr and Rb concentration as well as  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is evident for samples post-1950 as compared to pre-1950 due to thinning of annual layers

Table 2

Isotopic composition of Sr and concentration of Sr and Rb in sections of an ice core drilled at Mt Blanc, France

Section	ID	Type <sup>a</sup>	Year <sup>b</sup>	Depth <sup>c</sup> (m)	Sr (pg/g)	Rb (pg/g)	<sup>87</sup> Sr/ <sup>86</sup> Sr
23	2262	M	1990.0	21.9	51±1	21±1	0.7112±0.0007
	2261	M	1990.1	22.3	268±4	77±4	0.7109±0.0003
	2260	M	1991.2	22.5	1336±18	241±12	0.7107±0.0002
23		C	1990.4	22.2	427±6	90±5	0.7110±0.0005
39	1357	M	1986.5	38.6	2508±34	524±26	0.7114±0.0001
	1356	M	1986.4	38.8	553±8	63±3	0.7084±0.0007
	1355	M	1986.3	39.0	773±10	143±7	0.7107±0.0002
39		C	1986.4	38.8	1278±17	243±12	0.7102±0.0003
46	46	M, AP	1984.0	45.2	517±7	107±5	0.7176±0.0003
55	1711	M	1981.9	52.4	1130±15	343±17	0.7127±0.0003
	1507	M	1981.8	52.5	1760±24	549±27	0.7138±0.0002
	1496	M	1981.7	52.7	1961±26	529±26	0.7130±0.0003
	1494	M	1981.6	52.9	1593±22	742±37	0.7150±0.0002
	1493	M	1981.5	53.1	283±4	98±5	0.7118±0.0003
55		C	1981.7	52.7	1505±20	510±26	0.7135±0.0003
57	1320	M	1981.2	53.9	3190±43	960±48	0.7153±0.0002
	1319	M	1981.1	54.1	419±6	201±10	0.7196±0.0002
	1318	M	1981.0	54.3	18±0.3	7±0.3	0.7040±0.0012
57		C	1981.1	54.1	1209±16	389±19	0.7130±0.0005
69	69	M, AP	1979.0	61.2	72±1	27±1	0.7100±0.0007
71	71	M, AP	1977.7	62.9	508±7	171±9	0.7124±0.0006
80	80	M, AP	1975.8	69.4	680±9	175±9	0.7127±0.0002
88	88	M, AP	1972.6	75.7	1746±23	383±19	0.7118±0.0003
92	92	M, AP	1971.0	78.7	28±1	14±1	0.7119±0.0040
96	1670	M	1968.2	81.4	104±1	27±1	0.7094±0.0003
	1669	M	1968.0	81.6	64±1	13±1	0.7093±0.0005
	1667	M	1967.8	82.0	41±1	24±1	0.7127±0.0007
	1666	M	1967.7	82.1	84±1	30±2	0.7091±0.0008
96		C	1967.9	81.8	55±1	19±1	0.7049±0.0010
97	1728	M	1967.6	82.3	281±4	112±6	0.7114±0.0004
	1727	M	1967.5	82.5	476±6	92±5	0.7106±0.0002
	1726	M	1967.4	82.7	800±11	289±14	0.7099±0.0002
97		C	1967.5	82.5	566±8	175±9	0.7105±0.0003
98	1840	M	1967.2	82.8	99±1	24±1	0.7107±0.0005
	1839	M	1966.9	83.1	49±1	18±1	0.7098±0.0006
	1838	M	1966.8	83.4	143±2	74±4	0.7099±0.0007
98		C	1967.0	83.1	97±1	39±2	0.7101±0.0006
103	103	M, AP	1965.0	86.7	245±3	36±2	0.7102±0.0006
107	107	M, AP	1963.4	90.4	107±2	35±2	0.7100±0.0016
111	1883	M	1961.5	92.8	1954±26	463±23	0.7103±0.0002
	1882	M	1961.3	93.0	1187±16	236±12	0.7103±0.0002
	1880	M	1961.1	93.2	115±2	35±2	0.7108±0.0004
	2032	M	1960.9	93.4	23±0.4	20±1	0.7120±0.0025
	2031	M	1960.8	93.5	39±1	26±1	0.7157±0.0038
	2030	M	1960.7	93.6	222±3	45±2	0.7170±0.0007
	111		C	1961.1	93.3	684±9	159±8
112	1894	M	1960.6	93.8	119±2	71±4	0.7106±0.0004
	1893	M	1960.5	94.0	571±8	262±13	0.7104±0.0003
	1892	M	1960.3	94.2	244±3	53±3	0.7090±0.0008
112		C	1960.5	94.0	260±4	102±5	0.7099±0.0005
114	114	M, AP	1957.6	95.7	323±4	173±9	0.7124±0.0002
123	2120	M	1954.5	102.9	474±6	111±6	0.7102±0.0002
	2119	M	1954.2	103.2	124±2	88±4	0.7078±0.0017
	2118	M	1953.9	103.4	71±1	48±2	0.7020±0.0007
123		C	1954.2	103.2	259±4	86±4	0.7072±0.0008
131	131	M, AP	1945.0	108.6	208±3	78±4	0.7122±0.0004

(continued on next page)



Table 2 (continued)

Section	ID	Type <sup>a</sup>	Year <sup>b</sup>	Depth <sup>c</sup> (m)	Sr (pg/g)	Rb (pg/g)	<sup>87</sup> Sr/ <sup>86</sup> Sr
136	136	M, AP	1940.2	112.6	289±4	67±3	0.7117±0.0003
143	143	M, AP	1917.0	117.8	218±3	40±2	0.7098±0.0010
147	147	M, AP	1912.0	120.9	257±4	69±3	0.7117±0.0003
152	1762	M	~1885	123.7	249±3	49±2	0.7113±0.0003
	1761	M	~1885	123.7	162±2	32±2	0.7104±0.0002
	1760	M	~1885	124.2	71±1	19±1	0.7111±0.0005
152		C	~1885	123.9	161±2	33±2	0.7108±0.0003
156	156	M, AP	~1855	127.6	377±5	119±6	0.7124±0.0003
160	160	M, AP	~1800	130.6	390±5	88±4	0.7114±0.0006
167	167	M, AP	~200 BP	136.2	319±4	79±4	0.7118±0.0003

Uncertainties are 95% confidence intervals.

<sup>a</sup> M: measured sample, C: calculated weighted average of individual measurements, AP: aliquots of subsections pooled prior to analysis (see text).

<sup>b</sup> See text for discussion of dating. Decimal estimates of the dates are given assuming the snow accumulation to be constant within each section, using  $\delta D$  to identify winter/summer periods. The ages of the deepest samples are only approximate.

<sup>c</sup> The inner part of each core section (column 1) was broken into 0.1–0.4 m length subsections. The depth given is the upper extent of each section or subsection.

with depth. The deeper the sample in an ice core, the thinner it becomes due to compression by the snow and ice above and also by lateral flow. This means that for samples of the same thickness, deeper samples will integrate more time than shallower ones. Therefore, shallow samples are better able to resolve short-term or seasonal changes. Our pooled samples integrate ~2 yr from ~200 BP to 1925 AD. From 1925 to 1975, they integrate 0.4–0.8 yr and from 1975 to 1991 they integrate ~0.2 yr. The observed increase in variation as we move towards the present is most likely due to the change in sampling resolution as seasonal effects which were averaged out in deeper samples become resolvable in shallower ones. However, it is important to consider that the strength of seasonal effects may be influenced by anthropogenic emissions and it is likely that anthropogenic emissions have increased over time due to mining, smelting, industry and incineration, etc. Therefore, the increased variation observed post-1950 may be somewhat influenced by anthropogenic emissions.

The Rb and Sr concentrations show different trends before and after 1950. From ~200 BP to 1950 the concentration data are relatively constant. After 1950, the concentration increases towards the present. The post-1950 samples are uniformly distributed in time throughout each year and this helps to minimise any seasonal bias. Also, 2-yr averages have been calculated (see Fig. 1) to allow comparison of pre- and post-1950 data independent of seasonal variation. Measurements of Cd, Cu and Zn on the same samples also show constant concentrations in the ice until the end of the 19th century and then an increasing trend [16]. The Cd and Zn trend was attributed to increasing emissions

from Switzerland. Van de Velde et al. [2] also measured Ag, Au, Pt, Pd, and Rh in different aliquots of the same samples and their data show that natural source inputs (rock and soil dust, cosmic dust and seasalt spray) have not changed significantly over the period 200 BP to 1991. Instead anthropogenic inputs such as mining and smelting, and municipal incinerators are proposed as sources that have increased their emissions. The <sup>87</sup>Sr/<sup>86</sup>Sr isotopic composition trend has not changed along with the increases in Sr and Rb concentrations. The mean post-1950 <sup>87</sup>Sr/<sup>86</sup>Sr ratio (~0.712) is not significantly different from the mean pre-1950 <sup>87</sup>Sr/<sup>86</sup>Sr ratio. The Sr concentration has increased after 1950 but the <sup>87</sup>Sr/<sup>86</sup>Sr ratios have not changed suggesting that the anthropogenic emissions described above also exhibit a mean <sup>87</sup>Sr/<sup>86</sup>Sr ratio of ~0.712. The pre-industrial <sup>87</sup>Sr/<sup>86</sup>Sr ratio of ~0.712 is similar to that observed in samples measured in Greenland corresponding to glacial periods [20]. The ratio we observe in recent times is likely to be a mix of the pre-industrial sources, including natural sources of local and long-distance origin and various anthropogenic sources.

There is no clear evidence in the elemental or isotopic data to indicate any influence, e.g., by increased pollution levels, of the opening of the Mt Blanc tunnel to road traffic in 1965, although it is probably incorporated in the general increase of the element concentrations apparent after 1950.

### 3.3. Seasonal data

When the temporal resolution of samples is high enough to allow seasonal effects to be discerned it is

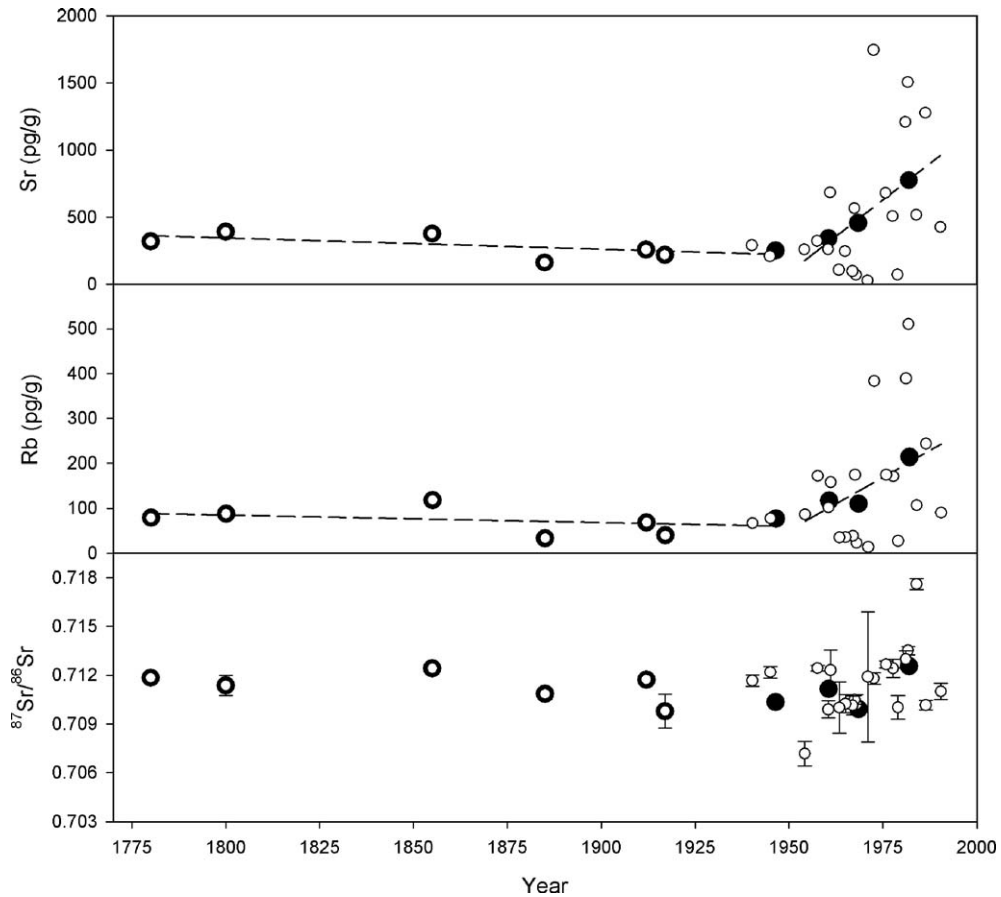


Fig. 1. The Sr and Rb concentrations and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio of samples in the 140 m Mt Blanc snow/ice core. Small open circles represent pooled data. Large filled circles represent data averaged over a 2 yr period. Uncertainties are 95% confidence intervals. For the concentration data, the uncertainties are smaller than the size of the symbols. Dotted lines are linear regressions.

possible to study both the impacts of sources and meteorology on the sample site. Fig. 2 shows  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{206}\text{Pb}/^{207}\text{Pb}$  [4] and Na/Al [3] ratios and normalised trace metal concentration data for the two high-resolution time-series sample suites from 1960 to 1961 and 1966 to 1968. Here a normalised relative trace metal concentration was determined as follows. For each of Al, Na, Pb, Ba, Rb and Sr a mean value was estimated for each of the two time series. Each elemental concentration for each sample was then expressed as a percentage enhancement (or reduction) with respect to the elemental mean. Finally these data were combined into a band (see Fig. 2B) to show the range of variation in the metal concentration data.

The normalised trace metal concentration data show similar seasonal trends in both periods. There were higher than average concentrations of Al, Na, Pb, Ba, Rb and Sr in spring/summer and lower than average concentrations in autumn/winter. This would appear to be due to changes in the vertical structure of the regional

troposphere as described by Van de Velde et al. [3]. Low-altitude thermal inversions occur frequently in the winter months and provide a barrier to the transport of ground based pollution emissions to higher altitudes. During warmer months the vertical transport of air is encouraged by convective storm systems and this promotes the free exchange of pollutants between altitudes. Indeed, the shielding provided by the inversions reduces pollution in the ice to levels comparable with those found in Greenland [3,4]. Our Sr and Rb concentrations support this observation.

The Na/Al ratios of samples from both suites (Fig. 2B) are similar and range from  $\sim 0.05$  to  $\sim 0.15$  except in autumn 1960 when there is a significant increase in the ratio to  $\sim 0.3$ . The Na/Al ratio of the upper continental crust is 0.36 [13] and the ratio for shales is 0.11 [14]. The samples vary in Na/Al ratio with their mean indicative of shales. This is to be expected since the neighbouring valleys of Mt Blanc are predominantly limestone and shale [21]. The lower values are

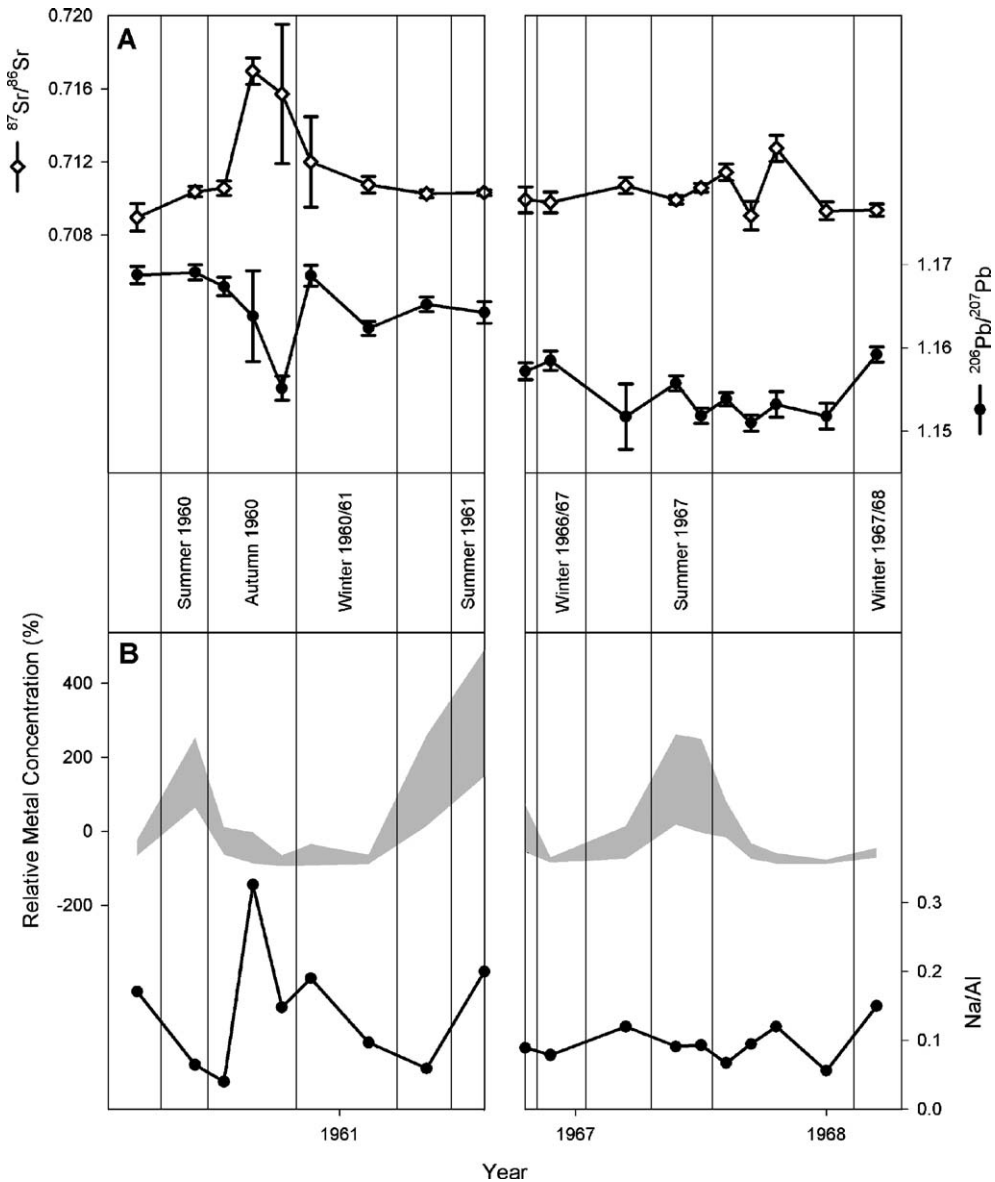


Fig. 2. Seasonal changes in the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic composition, Al, Na, Pb, Ba, Rb and Sr concentrations and Na/Al ratios.  $^{206}\text{Pb}/^{207}\text{Pb}$ , Pb and Ba data from Rosman et al. [4]. Na, Al data from Van de Velde et al. [3]. The seasons identified are based on temperatures inferred from D/H ratios [3] except Autumn 1960 which is inferred. See text for determination of relative metal concentrations. Uncertainties are 95% confidence intervals.

influenced by at least one other component with a lower Na/Al ratio, possibly anthropogenic pollution. The higher values probably reflect upper continental crust or oceanic sources.

The Pb and Sr isotopic data (Fig. 2A) are similar in character to the Na/Al data in that both seasonal data sets show consistent trends with the exception of autumn 1960. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios range from  $\sim 0.708$  to  $\sim 0.712$  but in autumn 1960 the ratio rises to as high as  $\sim 0.716$ . This would appear to discount the possibility

of an oceanic source as strontium derived from it has an  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic composition of  $0.7091 \pm 0.0001$  ( $2\sigma$ ) [18]. Rather, the high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio suggests an upper continental crustal source.

Van de Velde et al. [3] describe an event called a foehn which is an infrequent warm wind blowing from the south east during the winter months. This wind may have influenced the autumn 1960 sample composition. Although the foehn is infrequent it is likely to have a significant impact on the character of the sample



because the concentration of metals is relatively low during this period.

The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios appear to be lower in the 1966–1968 samples but this has been interpreted as characteristic of the period 1950–1968 and due to a steady change in the origin of lead added to petrol during that period [4]. However, the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of autumn 1960 samples ( $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.155$ ) deviates significantly from this trend and from surrounding samples ( $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.162$  to  $\sim 1.170$ ) indicating a different source of the aerosol. Rosman et al. [4] were unable to distinguish contributions of Saharan or Chinese aerosols which are both strongly affected by anthropogenic Pb, presumably from gasoline, and both are therefore possible. However, neither Chinese loess ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.726\text{--}0.728$  [10]) nor Gobi Desert sand ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.714\text{--}0.715$  [10]) provides as good a match as the range reported for Saharan dust ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.713\text{--}0.726$  [19]). The Saharan region has previously been identified as a predominant source of the dust input to Mt Blanc [21].

Furthermore Van de Velde et al. [16] observed an orange-brown layer in the ice at depth 54.1 m and dated 1981.1. It was concluded this was a consequence of the fallout of Saharan dust. Our Sr isotopic measurements of this particular section ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7153\text{--}0.7196$ ) confirm this conclusion. Also Rosman et al. [4] measured the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of the 54.1 m sample to be  $1.155 \pm 0.003$ . Both the Sr and Pb isotopic compositions of the 54.1 m sample, which is assumed to contain Saharan dust, are an excellent match for the Sr and Pb isotopic compositions of the autumn 1960 sample, suggesting that the origin of the autumn 1960 aerosol is Saharan.

#### 4. Conclusion

The Sr and Rb concentrations and Sr isotopic compositions have been measured in a 140 m snow/ice core from Mt Blanc using TIMS. These measurements are the first to record Sr isotopes in an Alpine glacier over a 200-yr period.

The 200-yr time series data show large variations in both concentration and isotopic composition. Strontium and Rb concentrations range from 3 ng/g to 20 pg/g and 1 ng/g to 10 pg/g, respectively, with higher concentrations evident in more recent times including a rising trend towards the present. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios vary between 0.7020 and 0.7176 with uncertainties of typically 0.0003 (but larger for smaller samples) allowing resolution of these differences. The mean  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $\sim 0.712$  is relatively constant throughout the time series with enhanced variation apparent in

recent times; however, this is largely due to increased sampling resolution. Glacial period samples from Greenland exhibit a similar  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $\sim 0.712$  indicating that the mixture of aerosol sources may be the same for both sites.

Data from the two high-resolution time-series sample suites from 1960–1961 and 1966–1968 show evidence of seasonal variation. The Sr and Rb concentrations follow the same trend as other metals in the same samples [2–4]. Seasonal variation in strontium isotopes is also apparent and it has been possible to provide evidence for the input of Saharan dust to the sampling site.

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