A ^{36}Cl PROFILE IN GREENLAND ICE FROM AD 1265 TO 1865

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ABSTRACT. We have measured the concentration of ^{36}Cl in 67 samples from the upper portion of the Camp Century ice core. The profile extends from AD 1265 to 1865 and covers the times of the Wolf (AD 1282–1342), Spoerer (AD 1416–1534) and Maunder (AD 1645–1715) minima in sunspot number. Although the profile exhibits much short-term variation, a smoothed plot of the data shows a strong peak in ^{36}Cl concentration over the time of the Maunder Minimum. The deeper part of the core suggests increased deposition of ^{36}Cl over the periods of the Wolf and Spoerer minima. The time resolution of the profile is inadequate for testing for an 11-year periodicity in our data. The data augment evidence from ^{10}Be and ^{14}C studies which indicate solar modulation of radioisotope production. Since, however, much of the short-term variation of ^{36}Cl seems to be independent of solar activity, other factors must affect the deposition of ^{36}Cl in ice. These variations could be due in part to mechanisms affecting the transport of ^{36}Cl in the atmosphere. Based on our data from Camp Century, we calculate an average input of ^{36}Cl of 24 atoms/m^2 sec.

INTRODUCTION

We have continued to measure ^{36}Cl in the Greenland Camp Century ice core (Conard *et al*, 1986; Elmore *et al*, 1987). The main goals of this work were to determine whether the deposition of ^{36}Cl in ice correlated with solar activity, as had been previously demonstrated with ^{10}Be (Raisbeck *et al*, 1981; Beer *et al*, 1984), and to test whether ^{10}Be/^{36}Cl values could be used for dating old ice (Nishiizumi *et al*, 1983). Our results from Camp Century (Elmore *et al*, 1987) indicate that the ratio of ^{10}Be to ^{36}Cl in ice varies greatly in a profile from AD 1570–1865, and that the decay of this ratio ($t_{1/2}$ = 370 kyr) will not be useful for dating ice. Similar results from the ETH in Zürich (Suter *et al*, 1987) verify this conclusion. Here we report data which extend the ^{36}Cl profile to AD 1265. The motivation for this work was to test whether ^{36}Cl in ice shows the same pattern of increase over the Wolf, Spoerer and Maunder minima that has been demonstrated with ^{14}C in tree rings and to approximately determine the input function of ^{36}Cl in global systems.

MEASUREMENTS

To study the history of ^{36}Cl deposition in a terrestrial reservoir, we obtained a nearly continuous section of ice from Camp Century, Greenland (77° 10′N, 82° 08′W). The chlorine in the samples was extracted in the form of AgCl as described elsewhere (Conard *et al*, 1986). The low chloride concentration in the ice necessitated the addition of chloride carrier. Typically, ca 1kg of ice was prepared, although samples as small as 100g were measured. For the part of the core younger than AD 1570, ice from individual tubes was prepared. These tubes each correspond to 4–6 years of snow accumulation, and therefore represent an average ^{36}Cl deposition over this time period. In the measurements of older ice, we often combined two tubes

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to reduce the short-term fluctuations in ^{36}Cl concentrations and to extend the profile further back in time with fewer measurements. These data points represent ^{36}Cl averages over ca 10 years. The upper portion of the profile contains some gaps where no ice was available for measurement and gaps that resulted from faulty sample preparation. The older part of the profile has only two short gaps where ice was not available.

The ^{36}Cl samples were measured on the MP tandem Van-de-Graaff accelerator of the University of Rochester as described elsewhere (Kubik *et al*, 1987). The uncertainties of the measurements reflect both uncertainties from counting statistics and reproducibility of several measurements of the same sample. Table 1 lists the tube numbers, ages and concentrations of the ^{36}Cl samples. These values are presented graphically in Fig 1A, B, where they are compared to Camp Century ^{10}Be data (Beer *et al*, 1984; Beer, pers commun, 1988) in Figure 1C for the same period (but a different sampling of the core), and ^{14}C calculated from tree-ring measurements (Stuiver & Quay, 1980) in Figure 1D. The age-tube correlation for the Camp Century data was determined using a flow model (Beer, pers commun, 1988). This time scale was then normalized using data from Johnsen *et al* (1972) which coincide with our depth profile. The time scale used here is the same as that used for ^{10}Be and ^{36}Cl profiles published earlier (Elmore *et al*, 1987) and contains an uncertainty of ca 10 years.

TABLE 1

List of ^{36}Cl samples measured in Camp Century Greenland ice core. Each sample is characterized by core tube number, age (AD), and ^{36}Cl concentration/g ice and associated measurement uncertainty.

No.	Year (AD)	^{36}Cl atoms/g ice (x10^3)
41	1862	3.75 ± 0.72
44	1852	1.61 ± 0.37
45	1848	2.65 ± 0.47
47	1841	1.39 ± 0.19
56	1810	2.51 ± 0.21
57	1806	3.49 ± 0.41
58	1803	5.46 ± 0.69
60	1796	1.86 ± 0.41
62	1789	0.56 ± 0.25
63	1785	1.36 ± 0.31
65	1776	1.92 ± 0.18
70	1761	4.04 ± 0.23
71	1757	1.64 ± 0.32
79	1733	1.51 ± 0.40
80	1730	1.25 ± 0.29
83	1720	2.56 ± 0.15
85	1711	2.79 ± 0.49
86	1707	3.61 ± 0.53
88	1700	2.78 ± 0.35
89	1695	3.00 ± 0.27
91	1687	2.61 ± 0.36

Table 1, cont'd

| No.	Year (AD)	³⁶Cl atoms/g ice (x10³)
93	1677	3.35 ± 1.07
94	1672	1.97 ± 0.33
97	1660	4.90 ± 0.31
98	1656	2.41 ± 0.22
99	1652	2.29 ± 0.18
100	1648	3.54 ± 0.53
103	1634	2.84 ± 0.22
105	1628	2.22 ± 0.44
107	1622	2.76 ± 0.31
109	1612	3.08 ± 0.33
110	1607	2.52 ± 0.23
111	1602	0.91 ± 0.38
112	1597	2.51 ± 0.35
113	1592	1.90 ± 0.40
115	1582	1.50 ± 0.19
117	1574	1.55 ± 0.16
119	1567	2.17 ± 0.56
120+121	1560	1.78 ± 0.12
122+123	1549	2.53 ± 0.20
124	1542	1.67 ± 0.57
125+126	1534	2.63 ± 0.66
127+128	1524	1.90 ± 0.30
129	1517	2.71 ± 0.23
131+132	1505	2.91 ± 0.15
133+134	1495	3.06 ± 0.19
135+136	1485	1.32 ± 0.25
137+138	1474	3.12 ± 0.29
139+140	1463	4.52 ± 0.55
141+142	1452	2.24 ± 0.16
148+149	1418	2.98 ± 0.18
150	1411	2.84 ± 0.33
151	1407	4.30 ± 0.35
152+153	1399	2.64 ± 0.22
154+155	1389	2.55 ± 0.15
156+157	1379	2.89 ± 0.13
158+159	1369	3.92 ± 0.17
160+161	1359	2.84 ± 0.12
162+163	1349	4.52 ± 0.39
164+165	1340	2.11 ± 0.21
166+167	1330	2.81 ± 0.15
168	1322	3.09 ± 0.37
169	1317	2.91 ± 0.32
170+171	1310	4.06 ± 0.36
172+173	1300	2.48 ± 0.13
174+175	1290	4.63 ± 0.30
178+179	1267	2.59 ± 0.14
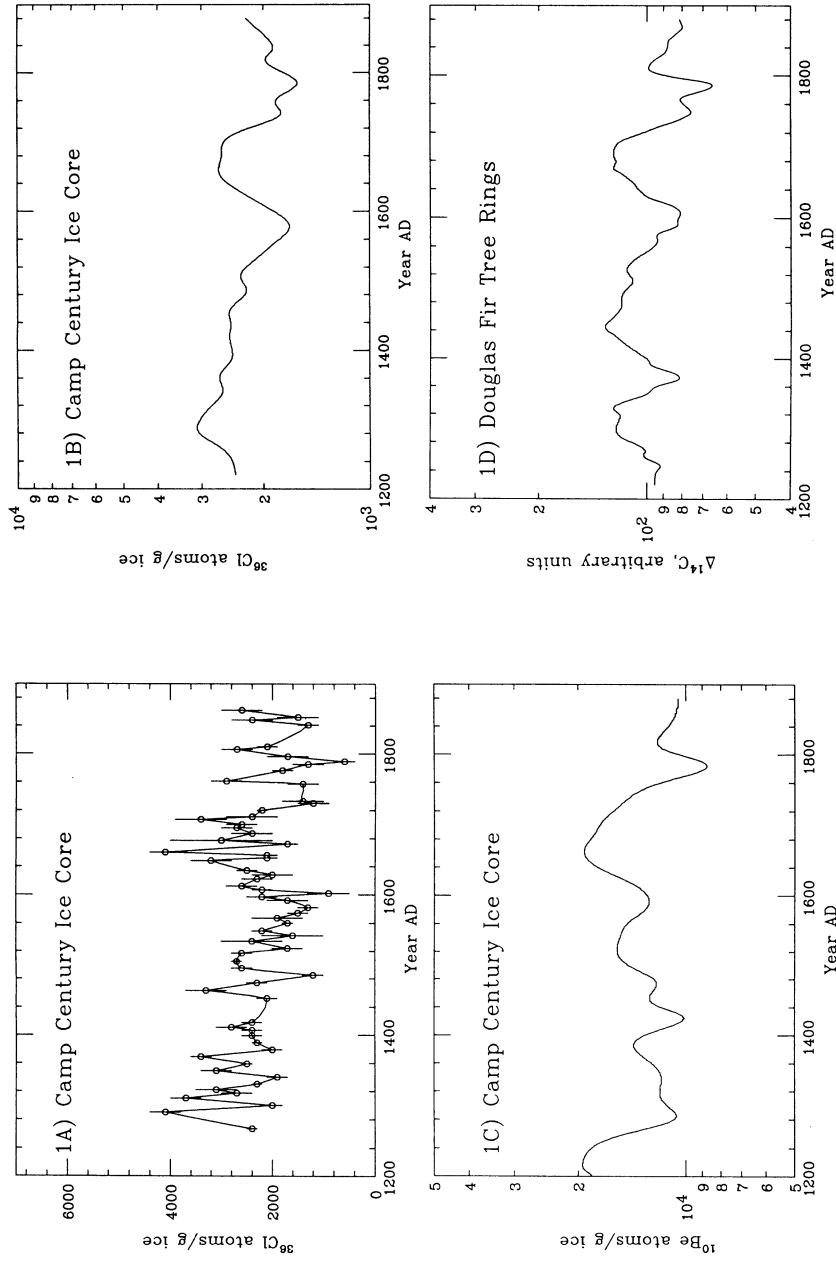
Fig 1. Profiles of ^{36}Cl, ^{10}Be and ^{14}C during the Wolf, Spoerer and Maunder sunspot minima (ca 1200–1900): A. Measured ^{36}Cl concentrations in Camp Century; B,C. Smoothed ^{36}Cl and ^{10}Be data using Gaussian weighting factor with mean width of 33 yr (3 solar cycles). The ^{10}Be data are from the same Camp Century, Greenland, core but from a different sampling and were measured at ETH Zürich (Beer, pers commun, 1988); D. $\Delta^{14}C$ calculated (Stuiver & Quay, 1980) from ^{14}C measurements of tree rings. The profiles 1B, 1C and 1D are presented on the same semi-logarithmic scale to facilitate comparison. A variation of a given factor is represented by a vertical line of the same length anywhere on all these plots.
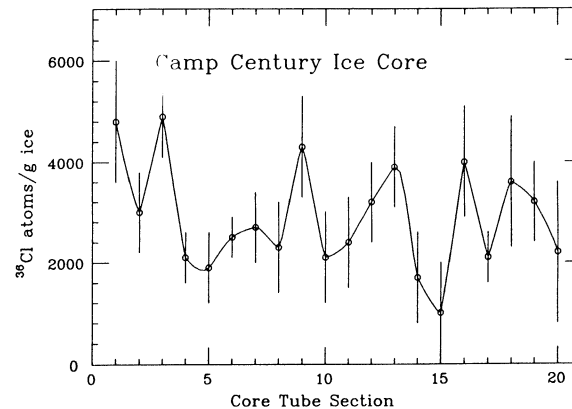
Fig 2. A continuous series of 20 ³⁶Cl concentrations from Camp Century tubes 168 and 169 (ca AD 1320). Each measurement represents ca 0.5 yr and was performed on ca 200g of ice. The measurements were made to test the feasibility of measuring very small samples and as a check for contamination, as mentioned in the text. This test shows that ³⁶Cl profiles in ice are measurable with high temporal resolution and can be performed on very small samples. The samples were not used up; the uncertainties could have been reduced with longer measurements.

In two samples, anomalously high concentrations of ³⁶Cl were measured previously; both samples were remeasured in new cuts of ice. The second ³⁶Cl measurements showed concentrations within the usual range of values. Since numerous chemistry blanks never showed high concentrations of ³⁶Cl, we believe that these instances of contamination were isolated and perhaps occurred prior to our chemical preparation. One of the samples (tubes 168 and 169, ca AD 1320) was cut into 20 sections to localize the suspected high concentration. The sections also served as a means to examine very short-term fluctuations in ³⁶Cl. Each section weighed between 85 and 335g and corresponded to slightly more than 0.5 years. In a very brief run, each sample was measured. Although the uncertainties of these measurements are high, they suggest that seasonal variations in ³⁶Cl can be as high as a factor of 3 (Fig 2). The measurements also indicate that high temporal resolution in ice cores measurements is possible.

DISCUSSION

As reported earlier for ³⁶Cl (Elmore *et al*, 1987) and ¹⁰Be (Beer *et al*, 1984) the profile of ³⁶Cl at Camp Century shows variability as high as a factor of 3 between individual samples and considerable short-term variability. To facilitate comparison of our ³⁶Cl data with the ¹⁰Be Camp Century data from Zürich, and with changes in production rates calculated for ¹⁴C, we have smoothed the data with a Gaussian weighting factor that has a mean width of 33 years (Fig 1B–D). This smoothing factor reduces the importance of short-term variation by averaging the data points over the period of three solar cycles.

The general trend of all three smoothed curves agrees fairly well, especially after ca AD 1500. The smoothed ^{36}Cl plot shows a strong peak over the region of the Maunder minimum. This peak-to-valley ratio is on the order of 1.5 as expected from calculations (Oeschger *et al*, 1970). The older portion of the profile shows generally high ^{36}Cl values over the Spoerer minimum and suggests a peak over the Wolf solar minimum; these correlations are, however, tenuous. In the regions of all three solar minima, both low and high values were measured, suggesting that factors in addition to radioisotope production affect the concentration of ^{36}Cl in ice. Although the strength of the geomagnetic field decreased over the time covering both Wolf and Spoerer minima, and therefore a corresponding increase in the radioisotope production rate could be expected (Beer *et al*, 1984) the ^{36}Cl concentration actually decreased by ca 30%. In addition, the great variability observed in ^{10}Be/^{36}Cl ratios from Camp Century (Elmore *et al*, 1987; Suter *et al*, 1987) indicates that transport mechanisms play a role in the deposition of radioisotopes in ice. While the sun's 11-year cycle should have contributed to the observed fluctuations of ^{36}Cl in ice, these fluctuations are far too large to be attributed entirely to solar modulation. The sampling interval of our profile is too large to test for the effects of the 11-year cycle using Fourier or other time series methods.

Future work with ^{10}Be and ^{36}Cl in glacial ice will need to address issues of transport and deposition modes. A study of the ^{131}I and ^{137}Cs fallout from Chernobyl (Clark & Smith, 1988) indicates that a higher ratio of halogens to metals can be expected in dry deposition than in wet deposition. Additional studies of transport mechanisms, such as sampling ^{36}Cl and ^{10}Be in air filters and precipitation, should be carried out to gain an understanding of the seasonal patterns of fallout. The results of our measurements from tubes 168 and 169 (Fig 2) show that very short-term variation in deposition can be studied with accelerator mass spectrometry.

Our data allow us to calculate the input function of ^{36}Cl at Camp Century. Based on a mean value in ice of 2700 ^{36}Cl atoms/g ice and a mean accumulation rate of 35cm/yr (Johnsen *et al*, 1972), we arrive at an input of 24 atoms ^{36}Cl/m^{2}sec over the period AD 1265–1865 at Camp Century. This number, when corrected for latitude dependence, can provide a useful estimate of ^{36}Cl input for groundwater studies. In the future, we plan to measure ^{36}Cl in precipitation at various sites to provide an accurate measure of contemporary input of ^{36}Cl in the atmosphere. The present value of 24 atoms ^{36}Cl/m^{2}sec falls within the range of calculated rates of ^{36}Cl input which range from 10–30 atoms/m^2 sec (Lal & Peters, 1967; Oeschger *et al*, 1970).

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