Reports

The Isotopic Composition of Methane in Polar Ice Cores

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Air bubbles in polar ice cores indicate that about 300 years ago the atmospheric mixing ratio of methane began to increase rapidly. Today the mixing ratio is about 1.7 parts per million by volume, and, having doubled once in the past several hundred years, it will double again in the next 60 years if current rates continue. Carbon isotope ratios in methane up to 350 years in age have been measured with as little as 25 kilograms of polar ice recovered in 4-meter-long ice-core segments. The data show that (i) in situ microbiology or chemistry has not altered the ice-core methane concentrations, and (ii) that the carbon-13 to carbon-12 ratio of atmospheric CH_4 in ice from 100 years and 300 years ago was about 2 per mil lower than at present. Atmospheric methane has a rich spectrum of isotopic sources: the ice-core data indicate that anthropogenic burning of the earth's biomass is the principal cause of the recent $^{13}CH_4$ enrichment, although other factors may also contribute.

ATMOSPHERIC METHANE IS A greenhouse gas second only to CO_2 in its effect on global temperatures: the atmospheric warming associated with the increase of CH_4 during the past decade is ~38% of the effect of CO_2 (*1*). The methane mixing ratio in trapped air bubbles in Greenland ice older than ~500 years is only half that of modern air (*1*). In 500- to 10,000-year-old ice the CH_4 mixing ratio is approximately 0.7 parts per million by volume (ppmv); in younger ice the mixing ratio increases rapidly to approximately the present atmospheric value in ice just below the firn layer. Studies of Antarctic and other Greenland ice cores have shown that this doubling of the CH_4 mixing ratio in trapped air is a ubiquitous feature in polar ice in both hemispheres (*2*). For at least the past decade methane has been increasing at a much faster rate, ~1.0 to 1.8% per year (*3*), and estimates of CH_4 mixing ratios in the atmosphere of AD 2050 have been made with a wide variety of scenarios with minimal constraints (*4*).

There are two ways to study the global production of methane. One is the comparison of rates of production by natural and anthropogenic sources with historical and ice-core records of the amospheric mixing ratio. The second is the study of variations in the isotopic composition of CH_4, including ^{13}C, ^{14}C, and deuterium-substituted molecules, in the atmosphere and in polar ice. Of these isotopic molecules only $^{13}CH_4$ can be measured in polar ice samples at present, and even measurements of this isotope require extraction and processing of ~0.002 cm^3 (standard temperature and pressure, STP) from large amounts of ice (~25 kg, representing ~4 m of core). Two important reasons for isotopic studies in ice-cores are (i) that the $^{13}C/^{12}C$ ratios of anthropogenic CH_4 sources vary over a wide range so that many of these sources are isotopically distinct; and (ii) because bacteria and chemical reactions tend to preferentially consume $^{12}CH_4$, it may be possible to show that the decrease in CH_4 mixing ratio with depth is not the result of in situ chemistry or biology in the ice.

One of us (*5*) measured $^{13}C/^{12}C$ ratios in atmospheric methane 35 years ago, but these older data are primarily of historical interest because CH_4 from liquid air plants was perforce used. Only recently, with the advent of high-precision techniques for sampling, processing, and analyzing small samples, have reliable data been obtained on atmospheric methane (*6*). The $^{13}C/^{12}C$ ratio of atmospheric CH_4 in 1980 [expressed in "δ" units as the ratio enrichment relative to the PDB standard (*5*)] was $\delta(^{13}C) = -47.7 \pm 0.2$ per mil (*6*). The uncertainty of ±0.2 per mil is based on measurements in 1978 to 1980 of 12 samples of air collected at Cape Meares, Oregon, and 7 samples from the Southern Hemisphere (*7*). At that time the isotopic composition was the same in both hemispheres; it was constant in the Northern Hemisphere from 1978 to 1983 and was increasing by 0.1 per mil per year in the Southern Hemisphere. A value of −47.8 per mil (Table 1) was measured on air collected in Greenland in 1983. Except for measurable hemispheric differences after 1980, the isotopic composition of atmospheric CH_4 is independent of latitude because of rapid intrahemispheric exchange [time constant = 2 months (*3*)] compared with the ~10-year atmospheric lifetime of CH_4.

Figure 1 summarizes the $^{13}C/^{12}C$ ratios in natural and anthropogenic sources of atmospheric CH_4 (*8*). The total range of ~50 per

Table 1. Isotopic analyses of CH_4 in 1983 Greenland air (GA-1 to -8), small samples of a CH_4 isotopic reference standard (STD), and CH_4 in two batches of He used as a purge in extracting CH_4 from melted ice. These data were used to determine the corrections in the analysis of CH_4 from ice samples for leak fractionation, addition of CH_4 in the stripping helium, and for the CO_2 impurity in the combustion train. The last column gives the final isotopic values with 1σ errors, relative to the Chicago PDB standard (*5*).

Sample	Air volume (liter, STP)	CH_4 volume (μl*)	Background $CO_2$$^+$ (%)	He-CH_4 correction (per mil)	Impurity CO_2 correction (per mil)	Final $\delta(^{13}C)$ (per mil)
GA-1	33.6	55.2	3	0	0	−47.86 ± 0.1
GA-2	2.22	3.68	17	0	0	−47.8 ± 0.3
GA-3	2.22	3.64	12	0	0	−47.5 ± 0.3
GA-4	2.36 air, 31 He	3.89	12	0	−0.7	−47.7 ± 0.3
GA-5	3 air, 30 He	5.5	8.4	−0.8	−0.5	−48.0 ± 0.7
GA-6	3 air, 6 He	5.1	8.8	−0.2	−0.3	−47.3 ± 0.7
GA-7	1 air, 66 He	2.2	25	−2.5	−1.8	−49.1 ± 0.7
GA-8	1 air, 66 He	2.3	21	−2.0	−2.0	−47.2 ± 0.7
CH_4–STD-1	—	1.6	15	0	0	−45.2 ± 0.5
CH_4–STD-2	—	1.7	18	0	0	−45.8 ± 0.5
CH_4–STD-3	—	5.3	17	0	0	−46.7 ± 0.5
He-1	66	0.8	50	0	0	−36 ± 2
He-2	66	0.5	18	0	0	−32 ± 2

*Measured as CO_2 after combustion.

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mil is very large, but almost all natural sources are depleted in $^{13}CH_4$ relative to atmospheric methane. Two major anthropogenic sources produce CH_4 depleted in ^{13}C by anaerobic bacterial processes (similar to those producing methane in wetlands): enteric fermentation in herbivores (mainly cattle) with $\delta(^{13}C) = -60$ per mil (*9*), and rice paddies with $\delta(^{13}C) = -67$ per mil (*8*). Most of the other anthropogenic sources produce relatively heavy methane: natural gas leakage at −44 per mil (*10*), coal mining at −37 per mil (*11*), and biomass burning with $\delta(^{13}C) = -25$ per mil (*8*).

Ice coring was done with a wire-line ice drill system developed for drilling and recovery of 4″ diameter ice core. The Dye 3 drill site was 1 km north-northeast of the Dye 3 base and 300 m north of the 1979 to 1981 deep borehole at 65°11′N, 43°50′W (*12*). Because of the extensive fracturing in the lower part of the Dye 3 core (*12*), an extra 8 m of core were drilled for us in 1985 at Site A, near "Crete" (~71°N, 37°W), at the bottom of a hole from 101 to 109 meters. This core was unfractured and provided two good samples.

Gas extractions were carried out in a large vacuum-tight pressure vacuum chamber cylinder with a plexiglass top for visibility. About 25 kg of ice, cut into large pieces, was used for each extraction. The cylinder was filled with ice in the cold room (−20°C), evacuated to the vapor pressure of ice, pumped and closed off, and the ice was allowed to melt, after which the gas sample was transferred through dry ice and liquid N_2 traps to a 33-liter baked and degassed Arco Spectra Seal aluminum cylinder by expansion followed by stripping with purified He. This gas was processed through a vacuum system in which the CH_4 was oxidized to CO_2 after separation of residual CO_2, CO, and nonmethane hydrocarbons (*13*). The final CO_2 from CH_4 combustion, 1.7×10^{-3} to 2.9×10^{-3} cm^3 (STP), was measured in a calibrated volume with an MKS Baratron gauge (MKS Instruments, Inc., Andover, MA) and transferred to a small sample tube for isotopic analysis.

The isotopic analysis of such small gas samples is critically important. The mass spectrometer standard was CO_2 with $\delta(^{13}C) = -45.9$ per mil, calibrated against a standard (−24.8 per mil), which had in turn been calibrated versus PDB (*5*). We also collected a large air sample at the Dye 3 site during our drilling in 1983, and samples of this air were used for checking all stages of the overall procedure: extraction of CH_4 from ice, combustion to CO_2, and isotopic analysis. Table 1 lists all the measurements on this Greenland air standard, including several 1- to 3-liter samples diluted with varying amounts of the helium used to extract the CH_4. The measured values of these samples (numbers 4 to 8) were 0.5 to 5 per mil more positive than the values for the undiluted samples because of a CH_4 impurity in the He and a small CO_2 blank in the processing system. The analyses of the small samples of the CH_4 isotopic standard (Table 1) served as an overall calibration for spectrometer inlet leak fractionation and change of isotopic composition during analysis.

The analyses of CH_4 in ten ice-core samples, including the various corrections applied to the raw data, and the final $\delta(^{13}C)$ values (*13*), are given in Table 2. The estimated precision of these data is ± ~0.7 per mil; it appears reasonable that this precision could be improved by about a factor of 2 in future efforts. Table 2 also shows the depth range of the 4- to 6-m core samples, the approximate CH_4 mixing ratio in the trapped air, and the estimated age of the ice in each sample, calculated from oxygen isotope stratigraphy and an empirical model (*14*).

Fig. 1. Measured $\delta(^{13}C)$ values of natural and anthropogenic methane sources (*8*). Open circles are the means of individual measurements, the ranges of which are shown by the bars. Complete references for the numbers of measurements and ranges are given in (*8*). Atmospheric CH_4 is enriched in $^{13}CH_4$ relative to the mean source value because the light isotopic molecule $^{12}CH_4$ reacts more rapidly with tropospheric OH radicals. The reaction rate is ~10 per mil greater for the light molecule, and about 88% of tropospheric CH_4 is removed by this process, resulting in an ~8 per mil enrichment of $^{13}CH_4$ in atmospheric CH_4. The remaining 12% of tropospheric CH_4 is removed by nonfractionating escape to the stratosphere where it is destroyed by similar reactions.

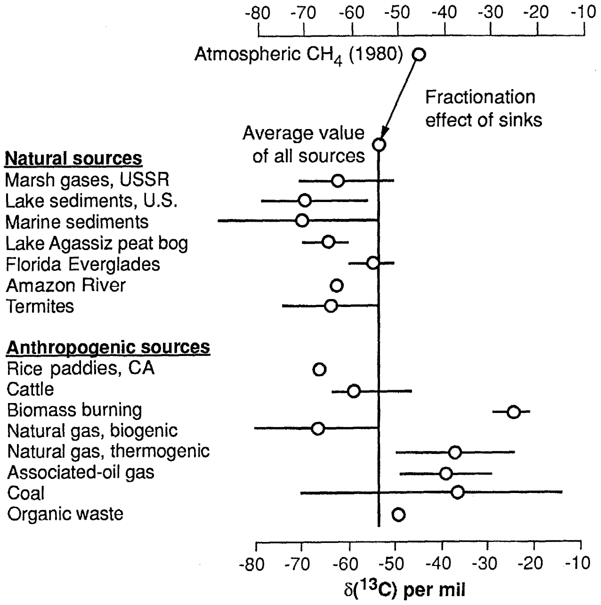

Figure 2 shows the $\delta(^{13}C)$ values and the ages of the ice-core samples. With the exception of two samples of "wafered" or highly fractured ice from the Dye 3 core, the $^{13}C/^{12}C$ ratio in methane from the two sites is essentially constant and depth independent, with a mean $\delta(^{13}C)$ of -49.6 ± 0.2 per mil. There are four wafered samples from Dye 3, three of which were analyzed when we thought these were the only deep samples we could obtain. The two suspect samples, at 193.5 and 198.0 m, are ~5 per mil enriched in ^{13}C relative to the other samples and have higher CH_4 mixing ratios. We performed two tests on the integrity of wafered ice. First, one ice sample (Dye 3, 178.5 m) was not pumped on in a vacuum to remove air, but had its air displaced by flowing helium through it in order to keep the sample at normal pressure. This sample gave CH_4 indistinguishable in concentration or isotope ratio from that of the unwafered samples. Secondly, we pumped on two small samples (25 g) of wafered ice for 0.3 to 1 hour in a vacuum system and then analyzed the remaining air in the ice after about 45% of the air had been pumped away. The residual air had preferentially lost O_2 (by 5% in both cases) and Ar (by 2.6 and 0.6%) relative to N_2. Pumping on unfractured ice produced no effect. This experiment shows that molecular processes can be important during loss by evacuation of air from sample containers in the case of severely fractured ice and that CH_4 might be held preferentially to other gases and even fractionated isotopically. Thus we attribute the results on the two anomalous wafered samples to effects of pumping on badly fractured ice. One other sample of wafered ice (Dye 3, 188 m) gave a value consistent with the data on unfractured samples for reasons not understood. Most of the ice obtained at these depths in the "shallow holes" is too badly wafered for trace gas studies. Fortunately the Site A core samples did not suffer from this problem and were of high quality.

A major question about the methane records in ice cores is whether in situ processes such as bacterial consumption or chemical reactions in the occluded bubbles may have consumed CH_4 in the older sections of the cores. Our isotopic data show that bacterial or chemical removal in the ice are not the cause of the 50% lower CH_4 mixing ratios in old polar ice. Isotopic fractionation in bacterial consumption and chemical reac-

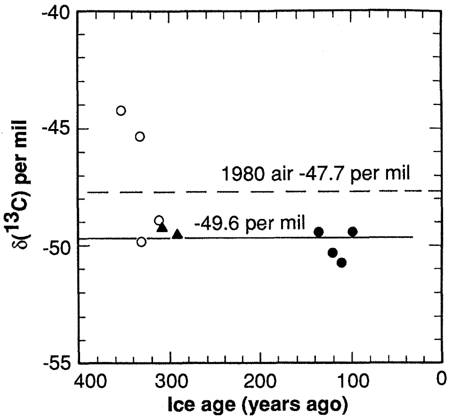

Fig. 2. $\delta(^{13}C)$ values of methane in Greenland ice versus age of the enclosing ice. Each sample represents ~0.002 cm^3 (STP) of CH_4 extracted from ~25 kg of ice. Triangles, samples from "Crete," Site A; circles, Dye 3 core samples; solid circles, solid ice; open circles, wafered ice. The means of the two groups of samples differ by only 0.6 per mil: −49.3 ± 0.2 per mil at 310 years, and −49.9 ± 0.3 per mil at 120 years. This difference is insignificant with respect to the mean value of −49.6 ± 0.2 per mil for the set of eight good samples and the ±0.7 per mil errors on the individual data points. [Errors for the two groups of samples and the total set refer to the means; uncertainty in $\delta(^{13}C)$ of 1980 air is ±0.2 per mil.]

tions removes the lighter isotope preferentially: either process would have left the residual CH_4 highly enriched in $^{13}CH_4$, both with respect to atmospheric CH_4 and along the core itself from the 100- to the 350-year-old ice. Methane in our oldest samples (Table 2) should be enriched in $^{13}CH_4$ by some 15 per mil [range 5 to 25 per mil on the basis of a survey of published fractionation factors; for example, (*15*)] relative to the present atmospheric value. This case is quite the opposite of what we observe and we conclude that in situ effects are not responsible for the isotopic record in these cores.

The age of occluded air might range from the actual age of the ice matrix to a much younger age corresponding to rapid mixing with the atmosphere in the firn layer (*1*). At Dye 3, and also at Crete, the firn-to-ice transition isolates the air completely at a depth of 68 m, corresponding to ice ages of ~90 years at Dye 3 and to 170 years at Crete (*14*), where the accumulation rate is only half as great (*16*). Thus we assumed (*1*) that trapped air at Dye 3 is as much as 90 years younger than the ice in which it is sealed. Schwander and Stauffer (*17*) reached the same conclusion. However, the isotopic data seem to preclude such a large difference in age between air and ice. As shown in Fig. 2, this large an age difference at Dye 3 would require an extremely steep rate of change: 2 per mil in isotopic composition in the last 10 years (that is, if the 100-year-old ice contains 10-year-old air). Such a large change seems unreasonable.

The isotopic data indicate that from approximately 300 ± 50 years ago to somewhere between 10 and 100 years ago, the $^{13}C/^{12}C$ ratio of atmospheric CH_4 did not change, although the atmospheric mixing ratio increased by ~50%. Then within the last several decades, the $^{13}C/^{12}C$ ratio increased by 2 per mil, from −49.6 per mil to the present-day value of −47.7 per mil, while the concentration increased by 33%.

Most of the global production of CH_4 is removed in the troposphere by reaction with OH radicals on a time scale of ~10 years, although a small fraction (~12%) leaks through the tropopause and is destroyed in the stratosphere. Isotopic fractionation in the OH reaction causes the steady-state $^{13}C/^{12}C$ ratio of atmospheric (atm) CH_4 to differ from the composition of its sources. The mean $\delta(^{13}C)$ value of the sources is therefore given by:

$$\delta_{source} = \delta_{atm} + F(\alpha^* - 1)(1 + 10^{-3}\,\delta_{atm}) \cdot 10^3$$

in which α^*, the isotopic fractionation factor for methane removal by chemical reactions, is the ratio of the $^{13}CH_4$ and $^{12}CH_4$ reaction rates k_{13}/k_{12} ($\alpha^* < 1$), F is the fraction of CH_4 removed by chemistry, and the δ's and $(\alpha^* - 1) \cdot 10^3$ terms are expressed in per mil. Ehhalt and Schmidt (*18*) calculated that the CH_4 residence time versus removal to the stratosphere is 77 years. Prinn *et al.* (*19*), using a new determination of atmospheric OH concentrations, calculated a mean tropospheric residence time versus oxidation by OH radicals of ~10 ± 2 years. Thus the total tropospheric residence time for CH_4 is $(1/10 + 1/77)^{-1} = 8.8$ years, and $F = 8.8/10 = 0.88$, close to earlier estimates of 0.90 (*18*).

Rust and Stevens (*13*) measured $\alpha^* = 0.997$. Recently, however, Davidson *et al.*, using a different technique (*20*), measured a much larger effect with a mean fractionation factor of $\alpha^* = 0.990$, that is, $(\alpha^* - 1) \cdot 10^3 = -10$ per mil, the value we adopt here (*20*). The mean isotopic composition of the CH_4 sources is then calculated to be 8.4 ± 1.8 per mil lighter (more depleted in $^{13}CH_4$) than atmospheric methane (Fig. 1), that is with $\delta(^{13}C) = -56.1$.

We calculate (*21*) that the actual mean CH_4 source has $\delta(^{13}C) = -55.4$ per mil, rather than the nominal value of −56.1 per mil derived for the steady-state case of constant CH_4 atmospheric mixing ratio. Three hundred years ago, however, with atmospheric CH_4 at the ice-core $\delta(^{13}C)$ value of −49.6 per mil, the mean source value would have been −58.0 per mil, or 2.6 per mil lighter than the present mean global source value, for the non–steady-state condition. This 2.6 per mil increase in the $^{13}C/^{12}C$ ratio of the global CH_4 source must be due to an increase in the anthropogenic contributions, the only sources sufficiently enriched in $^{13}CH_4$ to account for an effect of this magnitude. Because the atmospheric mixing ratio of CH_4 has doubled in the past 300 years, the composition of the added sources responsible for the isotopic shift in atmospheric methane should be about twice the difference between present and past sources, or ~5 per mil heavier (^{13}C-enriched) than the original source CH_4, that is, approximately −53.0 per mil (*21*), if the mean natural-source isotopic ratios and fluxes have not changed.

Table 2. Isotopic composition of methane in Greenland ice. Columns 5, 6, and 7 give the analytical corrections applied: the mass spectrometer background contribution to the analyzed CO_2 in percent of the sample, and the corrections to the CH_4 isotopic composition for the CH_4 blank in the stripping He and for the blank CO_2 in the combustion system, both in per mil. Column 8 lists the final isotopic delta values, relative to the Chicago PDB standard (*5*); the estimated precision of these values is ± 0.7 per mil (1σ), based on the contributions from all sources of error. Values in parentheses are considered suspect.

Ice depth* (m)	~Ice age (years)	CH_4† (ppmv)	CH_4 (μl, STP)	Background CO_2 (%)	CH_4 in He (per mil)	Blank CO_2 (per mil)	$\delta(^{13}C)$ (per mil)
				Dye 3 site			
75.0	101	1.18	2.61	7	−0.5	−0.6	−49.4
78.7	112	0.97	2.32	19	−0.7	−0.6	−50.7
83.7	122	0.93	2.40	13	−0.7	−0.6	−50.3
93.0	138	0.92	2.37	11	−0.5	−0.6	−49.4
178.5‡§	313	0.68	1.50	29	−0.8	−1.0	−48.9
188.0‡	332	0.70	1.36	30	−1.2	−1.0	−49.8
193.5‡	344	0.87	1.44	27	−0.7	−0.7	(−45.3)
198.0‡	355	0.87	1.44	27	−0.5	−0.6	(−44.2)
				Site A			
103.0	292	0.83	1.98	11	−0.6	−0.7	−49.5
107.0	310	0.90	2.06	14	−0.6	−0.7	−49.2

*Mean depth of 4-meter core samples (5 m at 178.5 and 193.5 m; 6 m at 188 m). †Approximate CH_4 mixing ratios, from measurements of CH_4 yield (column 4) and the amount of extracted air for each sample. ‡Wafered ice sample. §Ice sample was flushed with helium to remove air from the extraction system without the use of vacuum pumping.

The fluxes of CH_4 from cattle and rice, which are based on measured unit rates of emission and global agricultural production data, are the best known of all the anthropogenic sources: 120 ± 50 Tg/year (1 Tg = 10^{12} g) for rice (*22, 23*) and 78 ± 12 Tg/year for cattle (*24*). Estimates of the fluxes from the isotopically heavy sources are: solid organic waste, 50 ± 20 Tg/year (*25*), natural gas leakage, 35 ± 10 Tg/year (*23*), coal mining, 20 ± 8 Tg/year (*26*), and biomass burning, 30 to 100 Tg/year (*27*).

Biomass burning is isotopically the most important anthropogenic CH_4 source because it has the highest $^{13}C/^{12}C$ ratio and differs most from the mean source ratio (Fig. 1). Forest fires in temperate and boreal forests produce ~2.5 Tg/year of CH_4 (*28*). Although deforestation in Europe and North America would have decreased natural forest fires, the decrease is unlikely to have been more than 1 to 2 Tg/year in consideration of the regrowth of most of the North American forests and because a large fraction of U.S. forest fires included in the above estimate are caused by man. Biomass burning by humans is the flux most difficult to estimate: thus we have calculated the required flux from this source to make the mean isotopic composition of all sources equal to −53.0 per mil (*21*), given the mean flux estimates and isotopic compositions of all other sources (Fig. 1). Using the Davidson *et al.* (*20*) fractionation factor, we obtain a required flux for anthropogenic biomass burning of 49 Tg/year. (A flux of 125 Tg/year would be required for the older factor of 0.997.) This result is relatively insensitive to the uncertainties in the fluxes from organic wastes and natural gas leakage because these $\delta(^{13}C)$ values are not much different from the mean. Errors in estimating the small CH_4 flux from coal mining are insignificant, so that the uncertainty in the calculated flux from biomass burning is nearly proportional to the uncertainty in the flux from rice. The isotopic mean of the natural sources, $\delta(^{13}C) = -58.0$ per mil based on the Davidson *et al.* fractionation factor, is in better agreement with the range of −55 to −70 per mil observed for the natural sources of methane from wetlands than a value of $\delta(^{13}C) = -52.4$ per mil derived from the smaller fractionation factor of Rust and Stevens (*13*). Thus a CH_4 flux of 49 Tg/year from biomass burning is reasonable.

There are two other effects that may alter the calculated biomass burning rate. First, there is the question of possible fractionation effects in the firn layer, before the atmospheric gases are trapped in the ice. Craig *et al.* (*29*) have shown that observed isotopic enrichments of ^{15}N and ^{18}O in the Dye 3 ice core can be explained by gravitational separation of isotopes and gases in the continuous pore spaces of the firn column. This effect could have increased the CH_4 mixing ratio by 0.4% and the $^{13}C/^{12}C$ ratio by 0.3 per mil, so that the ice core $\delta(^{13}C)$ values, corrected for the gravitational enrichment, would be about −50 per mil. This would require an additional small increment of biomass burning to produce the present isotopic ratio, so that the required flux would be 51, rather than 49, Tg/year. Secondly, several authors (*30*) have recently proposed that the loss rate of CH_4 by reaction with OH radicals might have been 25% greater from 30 to 100 years ago, so that if the same anthropogenic source strengths are assumed, the atmospheric residence time in 1980 would have been only 5.6 years and the calculated flux for biomass burning in 1980 becomes 58 Tg/year. On the other hand, if the residence time is fixed at 8 to 9 years in 1980, the anthropogenic flux estimates are 21% too high and must be reduced. The required flux from biomass burning then becomes 52 Tg/year (if the same fractional reduction is assumed for all anthropogenic fluxes). The effect of the change in F, the fractional loss rate by OH reactions, is only 2 Tg/year of this total flux.

The $\delta(^{13}C)$ values for CH_4 in the 100-year-old ice differ by no more than 0.6 per mil from those in 300-year-old ice (Fig. 2). The higher concentrations (1.1 to 1.2 parts per million by volume) in these samples reflect the addition of anthropogenic CH_4 components, and the small change in $\delta(^{13}C)$ during this 200-year interval indicates that the increases from cattle and rice production were balanced isotopically by emissions from heavy isotopic sources. However, the 2 per mil increase in $\delta(^{13}C)$ during recent decades shows that the heavy methane fluxes are now increasing at a more rapid rate than the light methane fluxes. This effect must be attributed to CH_4 produced by biomass burning and the accelerated deforestation in recent decades. We have assumed that fluxes of the natural sources and their mean isotopic composition have remained constant during the past 250 years. It is possible that this assumption is not entirely valid: effects such as long-term changes in rainfall in the wetlands, increases in arctic swamplands, and draining of wetlands for agricultural purposes may have been significant. In any case, the isotopic measurements of CH_4 in polar ice cores provide strong evidence that anthropogenic biomass burning, a negligible source for hundreds of years, has now reached a rate of methane production equivalent to ~25% of the combined fluxes from the world's total cattle and rice production. Put in another perspective, the burning of the world's forests by humans is producing CH_4 at a rate of 40 liters (STP) per day for every person in the world.

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21. The nominal value is −56.1; however, because of the nonsteady conditions of atmospheric CH_4 in 1980 (for both concentration and isotopic composition), the average $\delta(^{13}C)$ of all sources was more enriched in $^{13}CH_4$ than the value based only on the fractionation factor, and is calculated to be −55.4 per mil. Part of the difference is due to the increasing concentration: if we assume that this increase is ~1.2%/year, then the total flux in 1980 was ~9% greater than for steady-state conditions, or 50 Tg/year more than simply twice the flux of 300 years ago, for equal atmospheric lifetimes. Furthermore, the isotopic drift rate of 0.05 per mil per year (*6*) shows that the average $\delta(^{13}C)$ of the anthropogenic fluxes is more enriched than in the case of steady-state conditions. The combination of these two effects makes the mean $\delta(^{13}C)$ of the anthropogenic sources about −53.0 per mil.
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Dynamics of a Second-Order Phase Transition: $P\bar{1}$ to $I\bar{1}$ Phase Transition in Anorthite, $CaAl_2Si_2O_8$

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Electron microscopic study of the reversible $P\bar{1}$ to $I\bar{1}$ phase transition in anorthite (transition temperature T_c = 516 Kelvin) shows that the antiphase boundaries (APBs) with the displacement vector $\mathbf{R} = 1/2[111]$ become unstable at T_c, and numerous small APB loops are formed. These interfaces are highly mobile, and their vibration frequency increases strongly with temperature. These observations suggest that close to T_c, breathing-motion–type lattice vibrations of the framework cause the two different configurations around the calcium atoms, which are related by a translation of $\mathbf{R} \approx 1/2[111]$, to interchange dynamically through an intermediate $I\bar{1}$ configuration. The high-temperature $I\bar{1}$ structure is interpreted as a statistical-dynamic average of highly mobile antiphase domains of primitive anorthite.

STRUCTURAL PHASE TRANSITIONS occur when a material changes its crystallographic structure as a function of temperature and pressure. The macroscopic properties also change at the transition. Hence, the study of phase transitions is of importance for various scientific and technological applications of these materials. Whereas in first-order transitions, the symmetries of the phases above and below the transition point bear no relation to each other, the symmetries of the phases involved in a second-order phase transition are characterized by a supergroup-subgroup relation. Furthermore, second-order phase transitions are easily reversible compared to first-order transitions. Ferroelectrics as piezoelectric components and as pyroelectric detectors are some of the technologically useful materials showing second-order phase transitions. Although considerable progress has been made toward a theoretical understanding of structural phase transitions at the microscopic level (for example, concerning symmetry properties, Landau theory, and the application of static renormalization group theory to critical phenomena), our knowledge of the dynamics of the second-order phase transition is incomplete. Such a transition is associated with the formation of antiphase domains (APDs) or twins below the transition temperature, T_c. Because the interfaces separating these domains are observable by diffraction contrast in an electron microscope, the dynamics of the transition process can be studied directly. However, the only known example so far of the application of this technique is the study by Van Tendeloo *et al.* (*1*) of the α-β transition in quartz. They showed that with increasing temperature, the α_1 and α_2 twin domains break up into smaller and smaller domains close to the transition temperature, T_c (= 846 K) and that the high temperature β phase is a statistical-dynamic average of small α_1 and α_2 domains. The domain walls are mobile at and above T_c.

We have observed a similar dynamical phenomena associated with the $P\bar{1}$ to $I\bar{1}$ phase transition in anorthite (An), $CaAl_2Si_2O_8$, a framework aluminosilicate belonging to the mineral group known as feldspars. Anorthite in solid solution with albite, $NaAlSi_3O_8$, forms the plagioclase series, which are common minerals in terrestrial and lunar rocks and meteorites. Brown *et al.* discovered this phase transition, which occurs at 516 K, using high-temperature single-crystal x-ray diffraction (*2*). Their work suggested that a certain group of x-ray reflections (*c* type: $h + k$ = even, l = odd; and *d* type: $h + k$ = odd, l = even; where h, k, and l are indices of lattice planes) disappeared above T_c. Subsequent x-ray and neutron-diffraction studies have shown that the *c* reflections do not completely disappear above T_c, but persist as diffuse reflections to high temperatures close to the melting point (*3*). Refinements of the crystal structure above T_c indicated that although the framework attains virtually $I\bar{1}$ (body-centered) symmetry, the Ca atoms remain essentially in two different structural sites, mimicking their original positions in low-temperature $P\bar{1}$ (primitive) anorthite (*4*). These data suggest that the transition is not a typical displacive transformation, where the entire structure, including the Ca sites, attains $I\bar{1}$ (body-centered) symmetry above T_c; as a result, the $I\bar{1}$ structure has been interpreted as either a space average or a time average of $P\bar{1}$ anorthite. The $P\bar{1}$ anorthite is characterized by *c*-type APDs separated by antiphase boundaries (APBs). These domains have the same crystal structure but are displaced with respect to each other by a vector that is not a translation vector of the crystal structure. Electron microscopic studies have shown that the APBs with the displacement vector $\mathbf{R} = 1/2[111]$, observed in dark-field by imaging through *c* reflections, disappear above T_c but reappear on cooling in their original positions (*5*). Although some type of reorganization of the calcium sites and

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