

degree of overlap between the two theories. Conventionally, contact electrification is explained in the physicist's language of electronic states and work functions differing between two materials. The chemist may prefer to speak of acid-base interactions between surfaces, but these also imply a degree of charge rearrangement at the interface, either involving protons (Brønsted acids and bases) or electrons, in the more general Lewis sense. If interacting surfaces are abruptly separated, some fraction of the charge may remain on the 'wrong' material; in other words, acid-base interactions (insofar as they involve an ionic component) may be a precursor to contact electrification. Lee<sup>12</sup> has previously suggested that surface acidity and basicity can be related to surface acceptor and donor states, thus linking the languages of chemistry and physics. Whereas work functions for metals can be measured reliably, they are not easily established for insulators, whose surface states are strongly affected by restructuring, defects and adsorbates. On the other hand, the acid-base nature of insulating surfaces can be readily determined, for example by wetting experiments<sup>13</sup>, and so these characteristics may serve as useful predictors of the sign and magnitude of contact electrification between insulators. Whichever view is preferred, it is clear that the surface treatment

renders the interface sufficiently asymmetric to achieve contact electrification and strong adhesion.

We suggest that this approach may lead to applications in forming exceptionally thin adhesive joints between mating surfaces of materials having the same or similar surface chemistries. □

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## Synchronous changes in atmospheric CH<sub>4</sub> and Greenland climate between 40 and 8 kyr BP

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ICE-CORE reconstructions of atmospheric methane concentrations for the past 220 kyr have revealed large variations associated with different climatic periods<sup>1-4</sup>. But the phase relationship between climate and methane has been uncertain because of dating uncertainties and the coarse sampling interval of available methane records. Here we present a high-resolution record of atmospheric methane from 40 to 8 kyr ago from the GRIP ice core in Greenland. Our improved resolution and dating allow us to conclude that the large changes in atmospheric methane concentration during the last deglaciation were in phase ( $\pm 200$  years) with the variations in Greenland climate. Our results confirm the previous observation<sup>3</sup> that methane increased to Holocene levels when much of the Northern wetlands was still ice-covered, lending support to the suggestion<sup>3</sup> that low-latitude wetlands were responsible for the observed changes. We observe oscillations in methane concentration associated with the warm periods (interstadials) that occurred throughout the glacial period<sup>5</sup>, suggesting that the interstadials were at least hemispheric in their extent. We propose that variations in the hydrological cycle at low latitudes may be responsible for the variations in both methane and Greenland temperature during the interstadials.

Past variations of atmospheric CH<sub>4</sub> concentrations can be reconstructed by analysing the composition of bubbles trapped in polar ice sheets. Air filling the pore space in firn is enclosed when firn sinters to ice. The enclosure occurs at a depth of typically 70 m below the surface in a slow, continuous process. This implies that the air in the bubbles is younger than the surrounding ice and that very fast (for example, seasonal) variations are smoothed by the slow enclosure process.

Several arguments support the reliability of the ice-core reconstruction of CH<sub>4</sub> variations within the experimental uncertainties<sup>6-8</sup>. Earlier measurements from Dye 3 (Greenland) and Byrd and Vostok (Antarctica) showed that glacial-interglacial climatic changes were accompanied by large variations of the atmospheric CH<sub>4</sub> concentration, and that a similar relationship might also apply to events of shorter duration like the Younger Dryas. There remained questions about the potential leads and lags between CH<sub>4</sub> and climatic signals, and about possible CH<sub>4</sub> changes accompanying the interstadial events of the last ice age in the North Atlantic region. The new GRIP (Greenland Ice-core Project) ice core obtained on the top of the Greenland ice sheet at Summit (72° 34' N, 37° 37' W, altitude 3,230 m) offers the opportunity to answer these questions owing to (1) good time resolution caused by the large accumulation rate (present-day 0.21 m-H<sub>2</sub>O yr<sup>-1</sup>) at Summit, (2) precise dating of the ice<sup>5</sup>, (3) a relatively short age difference between air and surrounding ice (210 yr, compared with 2,500 yr at Vostok under present-day conditions<sup>9,10</sup>), (4) an excellent ice-core quality and (5) the measurements in progress of various chemical compounds in the same core, which can provide additional information for the interpretation of the CH<sub>4</sub> record.

Measurements of methane concentration have been performed at LGGE using a wet extraction technique followed by gas-chromatographic analyses of the extracted air<sup>2-4</sup>. The contamination occurring with this technique has been reduced by replacing the grease sealing of the sample container by an indium seal; contamination averages now  $18 \pm 26$  ( $2\sigma$ ) parts per billion by volume (p.p.b.v.). The analytical precision (calibration + contamination) is on average 37 p.p.b.v. ( $2\sigma$ ), excluding the uncertainty of the standard gas.

Ice samples (83) were analysed every ~10 m between 1,330 and 2,270 m depth. This leads to a mean time resolution ranging from 100-200 yr (upper part) to 600-900 yr (bottom part). The timescale for the ice originates from ref. 11. The age difference between air trapped in the bubbles and the surrounding ice has been investigated carefully at Summit for present-day conditions<sup>9</sup>. For other climatic epochs, it was calculated with a semi-empirical model of firn densification<sup>10</sup>, taking into account the temperature dependence of the close-off density<sup>12</sup>. The model requires knowledge of the mean annual temperature and the snow accumulation rate at the drill site, both deduced from the GRIP  $\delta^{18}\text{O}$  profile<sup>5,11</sup>. The resulting air-ice age difference ranges from 210 yr in present-day conditions to 750 yr in full glacial

conditions. The duration of the bubble enclosure ranges from 20 to ~100 yr respectively.

The atmospheric CH<sub>4</sub> profile is plotted against depth and gas age, together with the GRIP isotopic record<sup>5,11</sup> in Fig. 1. The record follows the main features revealed by previous Antarctic and Greenland records: the glacial-interglacial doubling from 350 to 700 p.p.b.v., the high mean concentrations around 30–35 kyr BP and the remarkable oscillation during the deglaciation, which is shown by the GRIP record to be synchronous with the Younger Dryas. Surprisingly, the Younger Dryas CH<sub>4</sub> concentration minima at Vostok and GRIP are almost identical. The air enclosure duration at Vostok is theoretically 900 yr (ref. 10), so a smoothing of the atmospheric Younger Dryas signal, which lasts ~1,000 yr, is expected. As this is not observed, we suggest that the air enclosure happened faster at Vostok than assumed.

New and remarkable in the GRIP core is the observation of six oscillations between 40 and 28 kyr BP which were not depicted previously (by the Vostok profile for example), probably because of the coarse sampling interval in this part of the Vostok record. Each of these GRIP CH<sub>4</sub> oscillations is associated with an isotopic interstadial episode (labelled 5, 6, 7, 8, 10 and 11 in Fig. 1). The interstadials labelled 2, 3, 4 and 9 have a shorter duration (~500 yr) and are associated with less-pronounced CH<sub>4</sub> peaks (no peak for interstadial no. 9). This could be due to the limited depth resolution of methane measurements in this part of the record, which could also be the reason for the differences of the ratios of amplitudes between isotopic and CH<sub>4</sub> oscillations for the interstadials 5 to 11. An additional new feature coming from the GRIP record is the distinct CH<sub>4</sub> minimum in the early part of the Holocene at 8.2 kyr BP, associated with a drop in the δ<sup>18</sup>O record.

The differences between the CH<sub>4</sub> and isotope records are also remarkable. The first difference concerns the start of the deglaciation, where the isotope indicates a first slow temperature increase between 20 and 17 kyr BP, whereas the CH<sub>4</sub> level stays at low values until 16.5 kyr BP. Another difference is in the Bølling-Allerød period (14.45–12.7 kyr BP), when the isotope shows a decreasing trend while CH<sub>4</sub> is increasing. Finally, the start of the Pre-Boreal stage (11.5–10.0 kyr BP) also indicates a slow isotopic increase, when the CH<sub>4</sub> level is already at its maximum. These differences indicate that the slow isotopic changes are not reflected in the CH<sub>4</sub> profile. But we note that during the Bølling-Allerød period, palaeodata reveal a warming trend in eastern North America<sup>13</sup>, suggesting that the cooling pattern in Greenland may not reflect an hemispheric phenomenon.

The question of possible time lags between CH<sub>4</sub> and climate changes can best be addressed by the use of our results covering the deglaciation and the Younger Dryas. The two fast CH<sub>4</sub> and temperature increases at 14.45 and 11.55 kyr BP (ref. 5) and the decreases at 12.7 kyr BP are almost in phase. The observed CH<sub>4</sub> changes precede the isotopic shifts by 100–200 yr, but such differences still lie within the uncertainties linked to the temperature and accumulation rate changes introduced in the densification model and are therefore not significant.

The GRIP CH<sub>4</sub> profile brings new insights to the causes of the methane concentration variations. The scenarios proposed to date involve (1) fluctuations in the global wetland extent, (2) clathrate decomposition, and (3) variations in the atmospheric concentration of the OH radical. Photochemical model studies indicate that the changes in the oxidative capacity of the atmosphere probably amplified the changes in CH<sub>4</sub> concentration during the deglaciation, requiring, in any case a major change in the CH<sub>4</sub> source strength as a primary cause (see ref. 14 for a review). Clathrate outgassing could lead to several abrupt increases of the atmospheric CH<sub>4</sub> level, up to thousands of p.p.b.v., during the deglaciation<sup>15</sup>. Such features are not observed in the GRIP record although its time-sampling interval is a factor of ten better than the pre-existing records. Moreover, clathrate decomposition due to warming in permafrost regions<sup>15</sup>

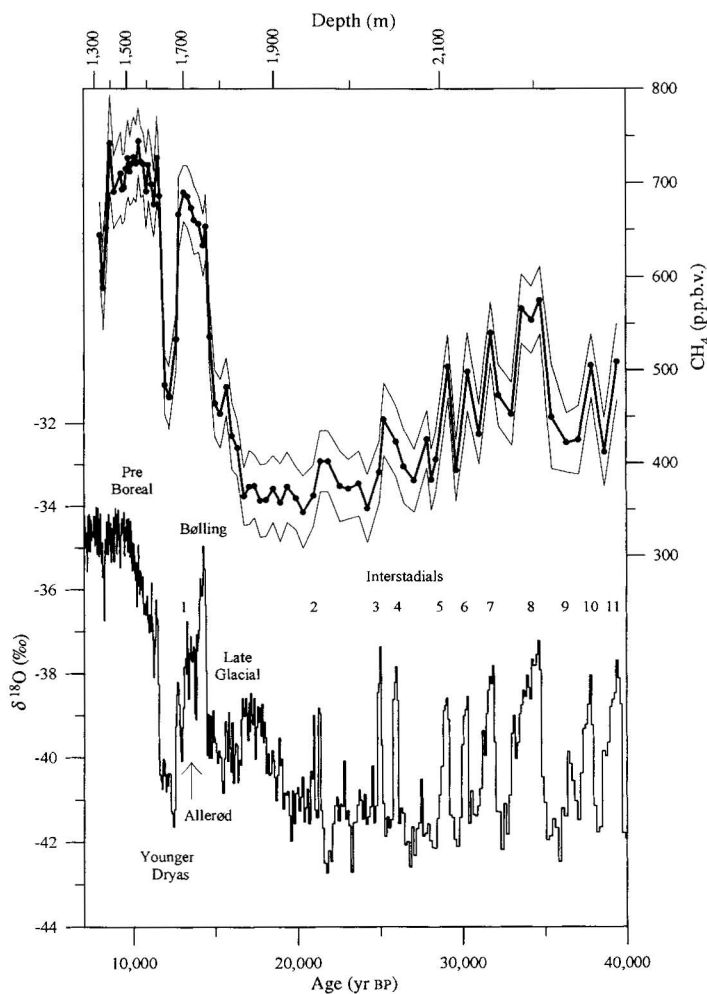


FIG. 1 GRIP ice-core profiles. Top, CH<sub>4</sub> record. The thick line runs through the mean concentration (black dots) and the two accompanying thin lines correspond to the experimental uncertainty ( $2\sigma$ ). Bottom, δ<sup>18</sup>O record along 2.2-m sections of the core<sup>5,11</sup>. The significant climatic events are noted by name or by suggested numbering<sup>5</sup>. The timescale applies to both records. The depth scale applies only to the CH<sub>4</sub> curve (top), because of the difference in age between trapped air and ice at a given depth. The CH<sub>4</sub> data are archived in the Ice Core Data Bank of the World Data Center-A for Paleoclimatology (NOAA, Boulder, Colorado).

would induce a CH<sub>4</sub> lag over the major Greenland warmings, which is not observed in the GRIP record. Although not ruled out, the hypothesis of catastrophic outgassing appears less probable. (It is, however, possible that clathrate outgassing contributed to smaller and slower CH<sub>4</sub> changes in the ice record.) On the other hand, we can quantitatively explain the deglacial CH<sub>4</sub> doubling by the moisture increase on the continents<sup>16</sup>. The relative role of high and low latitude wetlands in the control of atmospheric CH<sub>4</sub> levels is still questioned. But we note that CH<sub>4</sub> already reaches interglacial levels during the Bølling, when the Laurentide and Fennoscandinavian ice sheets were still largely extended. The CH<sub>4</sub> increase at the end of the last glaciation therefore leads the development of boreal vegetation and associated wetlands at high latitudes<sup>17</sup>, as for example depicted by the comparison with organic acid variations in the GRIP ice core<sup>18</sup>. Also, the two CH<sub>4</sub> oscillations (during the Younger Dryas and around 8.2 kyr BP) parallel two episodes of drought well marked in (for example) tropical Africa<sup>19–21</sup> and Tibet<sup>22</sup>. These observations reinforce the hypothesis that low-latitude moisture fluctuations play an important role in changes of atmospheric methane concentrations during the deglaciation.

The Greenland isotopic interstadials, as well as the Younger Dryas and 8.2 kyr BP droughts in the northern tropics are thought to result from changes in the formation of North Atlantic deep water (NADW)<sup>20,23</sup>, possibly linked to instabilities of the Laurentide ice sheet for the glacial episodes<sup>24</sup>. Therefore, the parallelism between the CH<sub>4</sub> fluctuations and the Greenland interstadial episodes depicted by our record would reflect an intimate connection between the North Atlantic thermohaline circulation and the hydrological cycle over the tropics, if the latter is effectively responsible for the major CH<sub>4</sub> changes. One possible mechanism to generate this connection could be a change in the evaporation rate over the tropical Atlantic, which would affect the advection of warm and saline subtropical water (towards the pole) and hence the NADW formation<sup>25</sup>, as well as precipitation over land. Such a mechanism could even account for a slight lead of the CH<sub>4</sub> increases over the Greenland abrupt warmings if the changes in evaporation and moisture at lower latitudes would first produce warm and salty water streaming north. A more detailed CH<sub>4</sub> record and progress on air dating can, together with coupled ocean-atmosphere models, help to find the basic mechanisms behind this emerging Greenland climate-methane connection.

As the interhemispheric mixing of the atmosphere is fast compared with the CH<sub>4</sub> changes observed in the GRIP ice core, the latter could be used to establish the link between the ice-core climatic records of the Northern and Southern Hemispheres. So far, the only GRIP CH<sub>4</sub> oscillation seen in the Antarctic ice is the Younger Dryas event in the Vostok profile. In order to synchronize the GRIP and Vostok (dating in ref. 4) Younger Dryas CH<sub>4</sub> oscillations, it is necessary to shift the Vostok oscillation by 1,200 yr (older), either by decreasing the air-ice age difference or by increasing the age of the ice. Uncertainties in these two quantities prevents attribution of the 1,200 yr shift definitely to one or the other. Moreover, re-dating the Vostok deglaciation would become easier with additional CH<sub>4</sub> measurements on this core.

The close relationship between atmospheric CH<sub>4</sub> concentrations and the Greenland isotopic temperature points to a strong biosphere-climate coupling on the secular timescale, and is in agreement with a positive CH<sub>4</sub> forcing on the climate. The magnitude of the CH<sub>4</sub> changes leads however, to a direct radiative impact of (at most) one-tenth of a degree<sup>3,7</sup> and therefore cannot be responsible for the abrupt shifts of several degrees recorded in Greenland. Additional CH<sub>4</sub> measurements on existing Greenland and Antarctic ice cores are still an important future objective, as they would help to clarify the crucial issues of (1) the phase relationship between the climatic events of the two hemispheres, (2) the interhemispheric CH<sub>4</sub> difference and its variations (that is an additional constraint for the causes of CH<sub>4</sub> changes) and (3) the geographical extent of the Greenland climatic flip-flops observed along the GRIP ice core<sup>11</sup>. □

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## Marine barite as a monitor of seawater strontium isotope composition

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THE strontium isotope ratio in sea water is influenced by climate, tectonics, weathering and hydrothermal activity at ocean ridges<sup>1–4</sup>. Its evolution through time, determined primarily by measuring the strontium isotope composition of marine carbonates, holds information about variations in these processes, and is also useful for stratigraphic correlation and dating<sup>5–7</sup>. Carbonates are absent from some marine sediments such as siliceous oozes and red clays, and can be significantly diagenetically altered in others, especially in Eocene and older sediments. Here we show that marine barite is an effective alternative monitor of seawater <sup>87</sup>Sr/<sup>86</sup>Sr. We find that microcrystals of marine barite separated from Holocene Pacific, Atlantic and Indian Ocean sediments all record the modern seawater <sup>87</sup>Sr/<sup>86</sup>Sr value. Moreover, the <sup>87</sup>Sr/<sup>86</sup>Sr of barite from 25 sediment samples spanning the past 35 Myr falls within the range of published data for carbonates over this time period. We conclude that marine barite reliably records both present and past variations in seawater strontium isotope composition.

The residence time of dissolved Sr in the oceans is 2–3 Myr, several orders of magnitude longer than the mixing time (~1,500 yr), and thus the Sr isotope composition is uniform throughout the world's oceans. Based primarily on measurements of carbonates, the seawater Sr isotope composition has been determined for the past 500 Myr of geological history<sup>8</sup>. The record is known in considerable detail for the Tertiary period<sup>9–11</sup> but, although the general features are known, becomes progressively uncertain further back in the geological record.

A limitation in using seawater Sr isotope composition for palaeoceanographic research is the availability and integrity of the recording material. Calcite is known to undergo recrystallization on burial, changing its chemical and/or isotope composition<sup>12–15</sup>. Furthermore, almost 50% of the ocean floor is covered with non-calcareous sediment. Therefore, identifying other phases that accurately record seawater Sr isotope ratio is an important goal. Marine barite, a widespread component of pelagic sediments<sup>16,17</sup>, may be such a phase. Within the rather large uncertainty limits available in the late 1960s, Goldberg *et al.*<sup>18</sup> showed that barite in surface sediments has the same Sr isotope composition as sea water.

Marine barite, in the form of microcrystals or aggregates of 0.5–5 µm size, is a ubiquitous minor phase of oceanic particulate matter and pelagic sediments<sup>19,21</sup>. It is particularly abundant in