

Effect of natural tetrafluoromethane

SIR—Tetrafluoromethane (CF_4), a potent greenhouse gas¹ with an atmospheric lifetime of at least 50,000 years (ref. 2), is believed to be of purely anthropogenic origin. Here we present evidence that about half the current atmospheric burden of CF_4 has accumulated naturally from weak, probably radiogenic, sources in the lithosphere. We detected significant traces of CF_4 in natural gas, and extracted appreciable amounts of CF_4 and SF_6 from a fluorspar (CaF_2), containing traces of uranium. Both gases could in future be used as geochemical tracers to yield information on fluid transport in the Earth's crust and on the evolution of natural gas deposits. Additionally, determination of the abundance of CF_4 and SF_6 in cometary or other planetary atmospheres could help to characterize the prevailing radiochemical conditions.

Earlier stratospheric measurements of vertical concentration gradients of CF_4 and C_2F_6 indicated that CF_4 could be a natural constituent of the Earth's atmosphere³. To test this suggestion, other measurements had to be carried out. The Paul Scherrer Institute (PSI) kindly provided sections of an ice core from Colle Gnifetti (4,450 m above sea level) in the Monte Rosa massif at the Swiss/Italian border⁴. For dating of the core sections, we used ^{210}Pb measurements as well as stratigraphic signals (for example, debris from volcanic eruptions), corrected for the 40 years needed to achieve gas closure (T. Blunier, personal communication). We carried out gas analyses at the Max-Planck-Institut für Aeronomie (MPAE) based on the existing gas chromatography/mass-spectrometer (GC/MS) system with prior cryogenic pre-concentration⁵. After melting about 1 kg ice in a pressurized glass cylinder with a stainless steel

top, we extracted dissolved gases using two different approaches: 'bubbling out' with synthetic air for core section BC144 (gas closure in 1790 ± 30); and 'salting out' with sodium chloride for two sections of BC123 (gas closure in 1860 ± 15). We obtained good agreement within the precision ($\pm 20\%$) of both methods. We determined the volume of air extracted from closed pores of the core sections using simultaneous GC/MS-measurements of ^{126}Xe . We found a mean value of 39 ± 6 parts per trillion by volume (p.p.t.v.) of CF_4 for the pre-industrial atmosphere.

In addition to these ice-core measurements, we analysed air from two sealed glass vessels at MPAE. One (sample AU/Gö) was a 3-litre glass bottle from the 1950s, the other (BM60) a 30-cm³ glass sphere from December 1960. We opened both vessels in a water bath to avoid contamination by ambient air, and found that they possessed interior pressures of less than 500 hPa, showing that both vessels remained airtight after their production from the hot glass melt. The CF_4 mixing ratios did not show a significant deviation from the ice-core measurements.

The figure shows the reconstructed chronology of CF_4 based on our stratospheric measurements⁵ and the results of this work. It also includes the two emission models A and B for which historic production numbers of primary aluminium are multiplied with emission factors for CF_4 (1.1 and 2.3 kg t^{-1} , respectively). Scheme A assumes our measured background concentration, whereas scheme B starts with an atmosphere free of CF_4 . A shows good agreement with all our measurements and requires a realistic emission factor, whereas B reproduces our observations very poorly.

Because it is extremely unlikely that the pre-industrial background of CF_4 was

produced by early activities of humans, we had to identify natural sources of CF_4 for a conclusive picture. When trying to measure the efficiency of thermal destruction² of CF_4 in flames of natural gas, we found excessive CF_4 in the exhausts. The cryogenic pre-concentration technique is not suitable for the measurement of CF_4 directly in unburnt natural gas. But because flames of ultra-pure synthetic methane in ambient air did produce excessive CF_4 , we are confident that surplus CF_4 in natural gas flames is not produced through recombination of thermally dissociated fluorocarbons, but is indeed present with about 700 p.p.t.v. in the burnt Russian natural gas. If this value is representative for the whole world, no more than 3 t CF_4 would be emitted annually by the combustion of natural gas. This source would thus be only a minor contributor to the annual atmospheric input of 15,000 t CF_4 through other anthropogenic sources such as aluminium production⁵.

Previous mass spectrometric measurements⁶ provided evidence that CF_4 can be produced in fluoride minerals by radiochemical processes. With GC/MS we analysed extracted gases from the same types of fluorspar (Wölsendorf) and could unambiguously identify CF_4 as well as SF_6 with abundances of several parts per million, whereas C_2F_6 was undetectable. This radiogenic production mechanism of CF_4 seems to be responsible for the existence of natural atmospheric CF_4 through cold degassing from the Earth's crust, with an annual rate of between 0.1 and 10 t yr^{-1} , which is negligible compared with the current anthropogenic emissions.

J. Harnisch

R. Borchers

Max-Planck-Institut für Aeronomie (MPAE),
Postfach 20,
37189 Katlenburg-Lindau,
Germany

P. Fabian

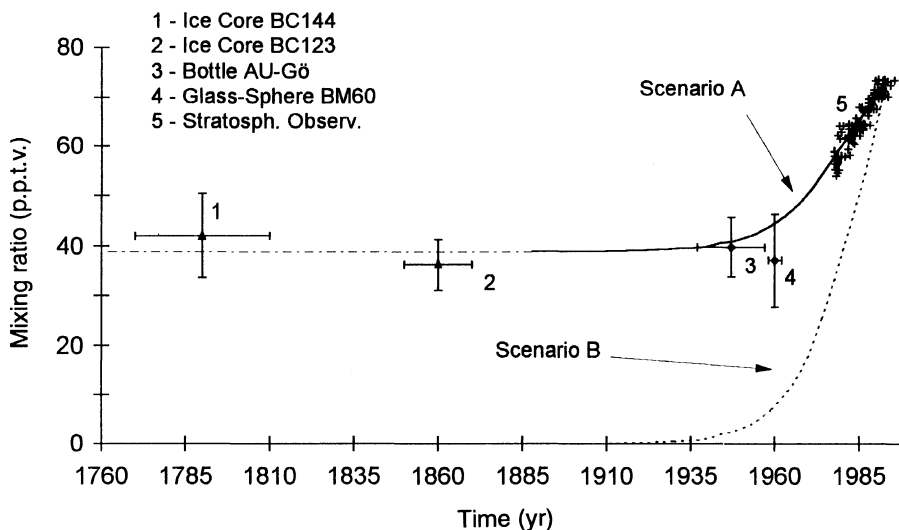
Universität München,
Lehrstuhl für Bioklimatologie und
Immisionsforschung,
Hohenbachernstrasse 22,
85354 Freising-Weihenstephan,
Germany

H. W. Gäggeler*

U. Schotterer

Paul-Scherrer-Institut (PSI),
5232 Villigen-PSI,
Switzerland

*Also at: Institut für Anorganische Chemie, Universität Bern,
Freie Strasse 3, 3012 Bern, Switzerland.



Reconstructed atmospheric chronology of tetrafluoromethane, with two emission models.

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