



## **A new ice core proxy of continental weathering and its feedback with atmospheric CO<sub>2</sub>**

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The analysis of CO<sub>2</sub> and its stable carbon isotopes from ice cores revealed large changes of atmospheric CO<sub>2</sub> which are closely related to a reorganisation of the global ocean circulation, marine processes and minor contributions in the terrestrial carbon storage. These components dominate the large CO<sub>2</sub> amplitudes during glacial/interglacial terminations. Yet, on longer orbital time scales, CO<sub>2</sub> is also modulated by the alkalinity of the ocean system. The net alkalinity influx to the ocean is driven by silicate weathering, which draws down atmospheric CO<sub>2</sub> and provides alkalinity in the form of bicarbonate ions. Conversely, alkalinity is lost during coral reef growth and when CaCO<sub>3</sub> is buried in marine sediments. On orbital time scales, these fluxes are assumed to be almost balanced as atmospheric CO<sub>2</sub> and its climatic effects feed back on the weathering rates providing a negative feedback loop.

Besides these basic concepts, little is known about the magnitude of weathering rate fluctuations on orbital time scales. To date, proxies from marine sediments and Fe-Mn crusts that faithfully record the ocean composition over glacial interglacial cycles do not quantify the total weathering fluxes to the ocean but only indicate that the style of weathering or the source area of sediment has changed. Due to large spatial heterogeneity, individual field site measurements do not elucidate global fluxes of weathering products to the ocean and how those might affect atmospheric CO<sub>2</sub> concentrations. Here, we use a novel approach using the pptv-level trace gas CF<sub>4</sub>, which can be analysed in air trapped in ice cores. CF<sub>4</sub> is a trace impurity in granites and other plutonic rocks, and during weathering this gas escapes into the atmosphere. In preindustrial times, weathering of granitic rocks was the only natural source of CF<sub>4</sub>. Because CF<sub>4</sub> is inert to destruction processes in the tropo- and stratospheres, its only sink is destruction by UV radiation in the mesosphere. This chemical inertness is responsible for an exceptionally long atmospheric lifetime which is expected to range between 50 kyr and 400 kyr.

We developed a vacuum melt-extraction system for ice core samples coupled to a mass spectrometry detector to precisely measure the trace amounts of CF<sub>4</sub> found in past atmosphere. During the last 800 kyr, the atmospheric CF<sub>4</sub> concentrations varied in a narrow band between 31 ppt and 35 ppt, i.e. only 10-15 % variability, providing a first estimate of the long-term weathering rate fluctuations. On closer inspection, our CF<sub>4</sub> record, however, shows a pronounced shift toward higher CF<sub>4</sub> levels after 430 kyr (the Mid-Brunhes Event). With the beginning of Marine Isotope stage 11, we find a steep rise in CF<sub>4</sub> that probably relates to intense weathering during the first interglacial, where CO<sub>2</sub> reached 280 ppm and sea level may have been even higher than today. Further, our record shows that CF<sub>4</sub> concentrations, and thus weathering, increases during interglacials and falls during the coldest, glacial phases. This dataset lends support to a strong positive coupling of continental weathering rates during warmer climate conditions at high CO<sub>2</sub> levels.