

Ice-core records of atmospheric composition and chemistry

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Ice cores record fundamental information about past atmospheric composition and chemistry, its intricate relationship with global climate, and recent changes to the atmosphere's composition due to anthropogenic activities.

As snow accumulates and compacts on ice sheets, ambient air is trapped within the ice, making glacial ice a direct archive of past atmospheric composition (McCrimmon et al. p. 112). The extraction and measurement of gases trapped in ice cores provide continuous, direct observations of atmospheric composition going back hundreds of thousands of years. These records show changes in atmospheric composition on timescales ranging from decades to hundreds of millennia (Martin et al. p. 100). Ice cores have provided high-resolution records of greenhouse gas (GHG) concentrations including carbon dioxide (CO₂) and methane (CH₄), and their influence on, and relation to, global climate.

In addition to trapped gases, ice cores also provide a unique archive of major ions and non-gaseous compounds including sulfate (SO₄²⁻), nitrate (NO₃⁻), and halogens (e.g. chloride, bromide, iodide); atmospheric acidity; and other measurements that provide information about atmospheric chemistry and anthropogenic pollution. In the following sections, we describe these ice-core records of Earth's atmosphere.

Long-term records of greenhouse gases

The fidelity of ice-core air as a record of past atmospheres is confirmed by the precise agreement between ice-core-derived records of GHGs and instrumental records over the last 40–60 years (Fig. 1a; Macfarling Meure et al. 2006). Ice cores from Antarctica have provided 800,000-year-long records of major GHGs in high resolution (CO₂, CH₄), covering eight complete glacial-interglacial cycles, with recent efforts aimed at recovering ice, and subsequently atmospheric composition, up to several million years old (Dahl-Jensen 2018). These data confirm that the modern atmospheric concentrations of GHGs and their rates of increase are unprecedented in at least the last 800,000 years.

Ice-core CO₂ records have established the fundamental relationship between atmospheric CO₂ and climate (derived from stable isotopes of H₂O in the ice surrounding the bubbles, which are temperature proxies; Wendt et al. p. 102) on glacial-interglacial timescales (Fig. 1a, c; Jouzel et al. 2007). GHG records on centennial and millennial timescales provide strong evidence of abrupt changes to Earth's climate system and atmosphere. For example, ice-core CH₄ records from Greenland and Antarctica reveal dramatic variability on decadal timescales that coincides with similarly abrupt

Northern Hemisphere climate changes recorded in Greenland ice cores, highlighting the sensitivity of CH₄ to abrupt climate change (Chappellaz et al. 1993).

Measurements of the stable and radioactive isotopic composition of atmospheric GHGs can reveal which sources contributed to changes in concentration over time. Because major GHG sources often have distinguishable isotopic compositions, variability in the strength of these sources over time had measurable impacts on the past atmospheric isotopic signature. Recently, the suite of trace gas measurements made on ice-core samples has expanded to include these isotope measurements, providing valuable constraints on the causes of past GHG variability and the complex dynamics of Earth's climate system. For example, records of stable isotopes in CO₂ suggest that land-based CO₂ sources caused abrupt CO₂ rises

during the last deglaciation (20,000–10,000 years ago), while ocean-based sources were responsible for a more gradual rise (Bauska et al. 2016). Records of CH₄ isotopes strongly suggest that changes in microbial sources, rather than abrupt releases of geologic CH₄, dominated the deglacial CH₄ change (Dyonisius et al. 2020).

Modern records of anthropogenic change

Ice cores preserve changes in atmospheric chemistry and pollution over human history (Wensman et al. p. 108). For example, they record how atmospheric sulfate, which causes acid rain and influences global climate, tripled between 1900 and 1980 due to fossil-fuel burning, and then declined from 1980 to present day following clean-air policies in North America and Europe (Mayewski et al. 1986; Fig. 2a). They also show how atmospheric nitrate concentrations have doubled since the 1950s due to increased

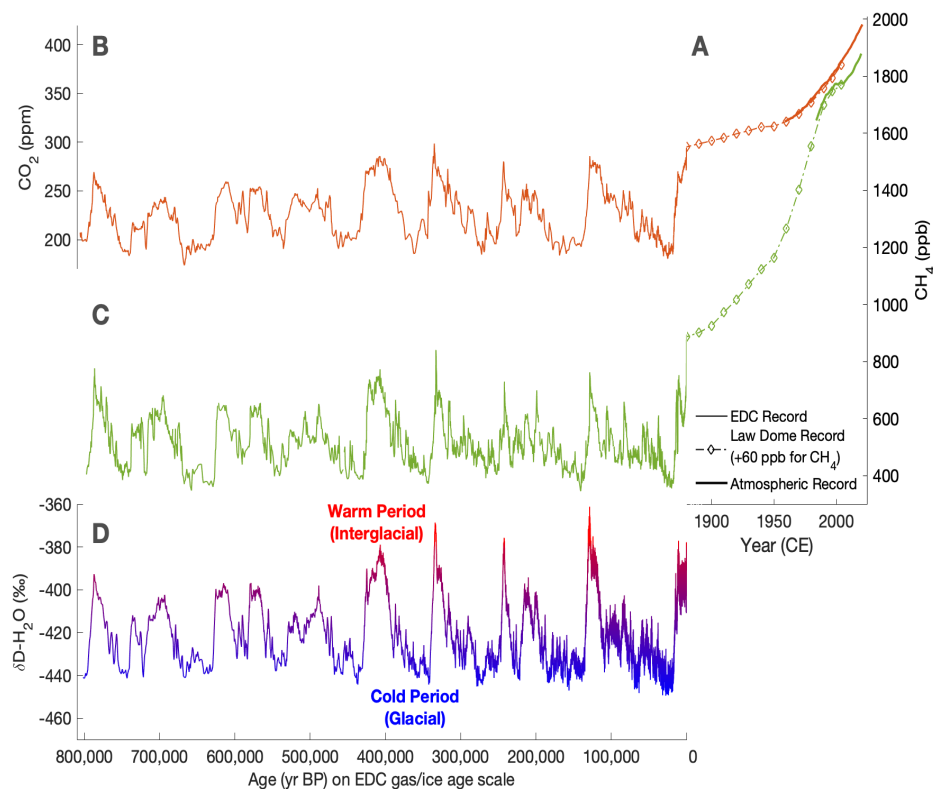


Figure 1: (A) CH₄ and CO₂ records from the Law Dome ice core (Macfarling Meure et al. 2006; dot/dashed lines) and the global mean atmospheric records (Hofman et al. 2006; solid lines) from 1875 to 2020 CE. In the modern atmosphere, Antarctic CH₄ is roughly 60 ppb lower than the atmospheric mean CH₄ because CH₄ sources are concentrated in the Northern Hemisphere. To account for this, the Law Dome CH₄ record was increased by 60 ppb. (B–D) 800,000 year Antarctic records of (B) CO₂, (C) CH₄, and (D) δD-H₂O, a proxy for temperature, all from the EPICA Dome C (EDC) ice core (Jouzel et al. 2007).

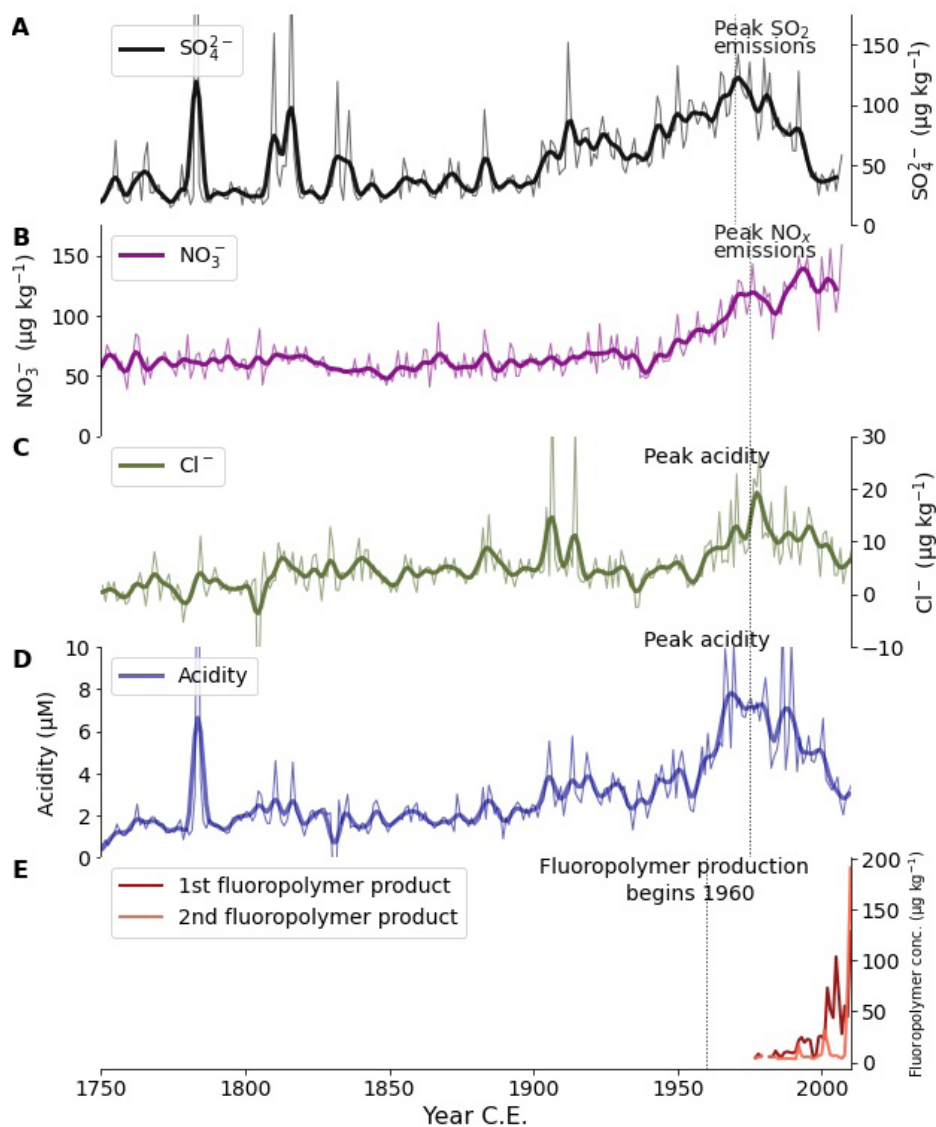


Figure 2: Recent measurements of dissolved ice-core species that tell us about atmospheric chemistry and pollution. Thin colored lines show annual measurements and bolded lines show multiyear averages. These ice cores are from the Greenland Ice Sheet and the Canadian Arctic. **(A)** Summit sulfate from Cole-Dai et al. (2013); **(B)** Summit nitrate from Geng et al. (2014); **(C)** Tunu chloride from Zhai et al. (2021); **(D)** Tunu acidity from Zhai et al. (2021); and **(E)** Devon Ice Cap and Mt. Oxford (northern Canada) perfluoroalkyl carboxylic acids from Pickard et al. (2020).

NO and NO₂ (collectively NO_x) emissions from fossil-fuel combustion and agriculture, which have changed the biogeochemical cycling of nitrogen since the pre-industrial era (Hastings et al. 2009; Fig. 2b).

Ice cores also provide information about the past and current abundance of atmospheric oxidants, which are chemicals that react with air pollutants (e.g. SO₂) and hydrocarbons (e.g. CH₄), yielding products that can cool (e.g. SO₄) or warm (e.g. CO₂) the atmosphere. These reactions can determine the lifetime of GHGs such as CH₄, so investigating how oxidants have changed can help estimate the warming potential of GHGs at different times in Earth's history. Although many oxidants such as ozone and the hydroxyl radical are too chemically reactive to be recorded in ice-core gas bubbles, proxies for these oxidants can indicate how oxidants have varied in the past. For example, clumped oxygen isotopes (i.e. ¹⁸O¹⁸O instead of ¹⁶O¹⁸O or ¹⁶O¹⁶O) constrain how ozone concentrations increased in the 20th century due to industrialization (Yeung et al. 2019).

Atmospheric halogens (elements including chlorine, bromine, and iodine) are some of the most reactive oxidants in the atmosphere and influence important species such as sulfate, volatile organic compounds, mercury, and ozone. It is difficult to know how atmospheric halogens have varied because measurements of reactive halogens have only been possible in the past few decades, but ice-core records combined with models can provide insight into how atmospheric halogen chemistry has changed due to anthropogenic pollution. For example, ice-core records of chlorine excess (i.e. chlorine that comes from a source other than sea salt; Fig. 2d) show how chlorine is correlated with atmospheric acidity (Fig. 2e) since the pre-industrial, and atmospheric models indicate this correlation is due to acidity reacting with sea-salt aerosols (Zhai et al. 2021).

Ice cores also record pollutants that only exist due to anthropogenic activities. Figure 2e shows ice-core concentrations of perfluoroalkyl carboxylic acids, which are byproducts of refrigerants that have been found in ice

cores starting in the mid-20th century and increasing rapidly after 1990 (Pickard et al. 2020). Records of these pollutants, along with concentrations of short-lived species such as sulfate, nitrate, and halogens, show how profoundly human activities have affected the chemistry and composition of the atmosphere, especially in the past 100 years.

Conclusions

Ice-core records provide unique archives of past changes in atmospheric composition and chemistry due to natural and anthropogenic causes. Ice-core gas records have provided information about past GHG concentrations and their relationship with global climate on glacial-interglacial and millennial timescales, as well as unprecedented increases in GHGs over the last century due to fossil-fuel burning. Analyses of major ions and other non-gaseous compounds have improved our understanding of anthropogenic pollution and its influence on atmospheric chemistry and climate. As older ice-core records are recovered and measurement techniques continue to improve, so too will our knowledge of past atmospheric composition and its interaction with climate and chemistry—knowledge that is essential for understanding the modern climate system and predicting future change.

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