

## Histories of Halogenated Strong Greenhouse Gases from Ice Cores, Deep Firn and Air Archive Records

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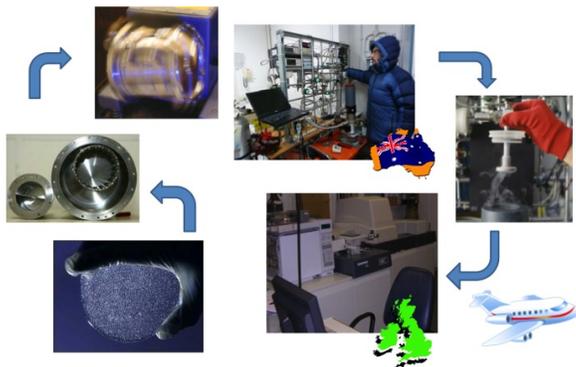
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Air extracted from ice cores and from firn offer the means to study the gaseous composition of the atmosphere before the time of instrumental records or “archiving” of whole air samples. We have examined a variety of halocarbons in ice from Law Dome, Antarctica, and in firn from several polar locations. Very high sensitivity techniques are required to determine halocarbon abundances in ice cores, as typically only a few tens of cm<sup>3</sup> of air can be extracted from each sample. Using a magnetic field sector mass spectrometer we are able to measure selected CFCs, halons, SF<sub>6</sub>, and perfluorocarbons (PFCs) in the ice at sub-pmol mol<sup>-1</sup> abundances. A unique feature of the ice drilling location at Law Dome is the high snow accumulation rate, and therefore narrow distribution of ages in air extracted from firn and ice, enabling relatively short-term (multi-year) features to be observed. After surveying a number of species measured in ice and firn, we then report on three of the PFC species (CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>) measured in glacial and also in archived air (Cape Grim, Tasmania). Using two independent firn diffusion models, and an atmospheric inversion calculation, it was possible to reconstruct continuous histories of these gases from the early 20<sup>th</sup> century to 2014. We were able to confirm that CF<sub>4</sub> has a natural emission flux, whereas this is undetectable for the other two gases. Emissions of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> exhibited a peak during WWII, doubtless associated with wartime aluminium production, followed by sustained increases post 1960 to annual emission rates that dwarfed those observed during the war years. Emission rates for all three gases have, however, declined substantially since at least 2000 (the early 1980s for CF<sub>4</sub>). Moreover there has been a large reduction in PFC emissions per kg of aluminium production, presumably due to better management of the production process (this can be determined up to the point when emissions from semiconductor manufacture became important). There is a substantial gap between calculated “bottom-up” emissions based on inventory estimates, and “top-down” estimates based on these reconstructed histories.



**Figure 1.** Air trapped in bubbles in glacial ice is extracted with a shaken “cheesegrater” device and collected in cold-fingers at ~10K at the CSIRO-CMAR laboratories in Melbourne, Australia, and subsequently analysed at UEA in Norwich, UK with a gas chromatograph/tri-sector mass spectrometer combination.