

Ground-truthing Electrospray-Orbitrap oxyanion isotopologue ratios: towards ice core clumped isotope palaeo-oxidation proxies?

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Modern gas-source mass spectrometers and optical spectroscopes enable clumped isotope analysis of simple gaseous molecules like CO_2 , O_2 and CH_4 . These new clumping measurements have become powerful paleo-environmental proxies due to their unique sensitivity to the pathways and conditions of molecule formation, as well as their independence from bulk isotope ratios [1,2].

Clumped isotope measurements require the analysis of intact molecules, so gas-source instruments cannot be applied to dissolved species like oxyanions and organics. In ice core archives, the clumped isotopes of these soluble molecules are thought to contain key information that can reveal past oxidation pathways in Earth's atmosphere. These insights may help unlock the elusive connection between climate and atmospheric chemistry, ultimately improving our ability to predict air quality and radiative forcing in a changing climate.

Recently, the Electrospray-Orbitrap mass spectrometer (ESI-Orbitrap MS) has been showcased as the upcoming new tool for stable isotopologue and clumped isotope analyses of intact soluble molecules. Its soft-ionisation and high mass-resolution enable, for the first time, simultaneous quantification of an extended range of singly and doubly substituted isotopologues of NO_3^- or SO_4^{2-} using just tens of nanomoles of sample – an improvement of 1-2 orders of magnitude [3,4,5].

Despite its impressive potential, questions remain regarding the accuracy, precision and robustness of ESI-Orbitrap MS measurements compared to the established IRMS and ICP-MS methods for NO_3^- and SO_4^{2-} stable isotope ratios in natural samples. To quantify its performance, we present a thorough intercomparison between ESI-Orbitrap MS and traditional bulk isotope measurements of the same ice core and aerosol samples.

Additionally, we present brand-new isotope clumping measurements of atmospheric NO_3^- and SO_4^{2-} archived in mid-to-low-latitude ice cores and invite suggestions towards the interpretation of these new palaeo-atmospheric proxies.

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