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Poster Session Day 2

Oxygen isotope analysis of nano-mole phosphate using PO_3^- fragment in ESI-Orbitrap-MS

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The oxygen isotope composition of phosphate is a useful tool for studying biogeochemical phosphorus cycling. However, the current Ag_3PO_4 method is not only tedious in PO_4^{3-} extraction and purification, but also requires a large-sized sample at the micromole level, thereby limiting its application. Here, we present an approach to measuring the oxygen isotope composition, $\delta^{18}O$, of dissolved phosphate at the nano-mole level using Electrospray Ionization Orbitrap Mass Spectrometry (ESI-Orbitrap-MS). We compared the reproducibility of $\delta^{18}O$ measurements using the $H_2PO_4^-$ ions (m/z=97 and 99 for $H_2P^{16}O_4^-$ and $H_2P^{18}O^{16}O_3^-$, respectively) and using the PO_3^- fragment ions (m/z=79 and 81 for $P^{16}O_3^-$ and $P^{18}O^{16}O_2^-$, respectively) generated by source fragmentation and by Higher-energy Collisional Dissociation, respectively. The results demonstrate that phosphate δ18O can be more reliably measured by the PO_3^- ions than by the $H_2PO_4^-$ ions. PO_3^- generated by source fragmentation at 40 V achieved the highest reproducibility for $\delta^{18}O$ based on precision tests. Furthermore, the mass spectrum for a 50μM:50μM mixed solution of phosphate and sulfate revealed that PO_3^- ions resulting from source fragmentation at 40 V are the predominant species in the Orbitrap analyzer. Notably, $P^{16}O_3^-$ ions (m/z: 79) are not interfered with by $^{32}S^{16}O_3$- (m/z: 80) ions. This is in contrast to $^1H_2P^{16}O_4^-$ ions, which share the same m/z value with $^1H^{32}S^{16}O_4^-$ ions and exhibit much lower signal intensity than HSO_4^- ions. Using the PO_3^- fragment method and six phosphate standards with a wide range of $\delta^{18}O$ values, we obtained a calibration line with a slope of 0.94 (R^2 = 0.98). The overall uncertainty for ESI-Orbitrap-MS phosphate $\delta^{18}O$ measurement was 0.8‰ (n =30; 1 SD). With much room for improvement, the PO_3^- fragment method presents a better approach to measuring the phosphate oxygen isotope composition, applicable to nano-mole sample sizes in a liquid phase.