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A N_2O-based cryogenic method for high precision, small sample size analysis of triple oxygen isotope composition by TILDAS laser spectroscopy

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Over the last decade, thousands of papers have been written about triple oxygen isotopes in natural materials. Early applications measured O_2 gas for the combined $^{18}O/^{16}$ and $^{17}O/^{16}O$ ratios using conventional gas source mass spectrometry. CO_2 gas could not be measured because of the interference of $^{12}C^{17}O^{16}O$ by $^{13}C^{16}O^{16}O$. More recently, triple isotope composition of CO_2 (evolved from carbonates or equilibrated with water) are measured using laser spectroscopy. This method involves measuring the intensity of specific $^{12}C^{16}O^{16}$, $^{12}C^{17}O^{16}O$ and $^{12}C^{18}O^{16}O$ absorption bands. CO_2 gas is diluted with N_2 gas in order to induce peak broadening for better peak fitting. Multiple aliquots of sample and reference gas are sequentially admitted into the laser cavity for high precision sample-reference comparison. Each gas aliquot is pumped away following analysis. Precision and sample size is limited by the need for multiple analyses with multiple gas aliquots.

In this work we substitute N_2O for N_2 as the diluting gas. N_2O (as well as CO_2) can be quantitatively frozen out at liquid nitrogen temperatures, so that a sample gas can be admitted into the laser cavity, analyzed and then frozen back into a cold finger for subsequent analyses. In theory, a single aliquot of gas can be analyzed infinite times to achieve high precision with samples as small as 25 microgram calcite equivalent. We have tested this method on an Aerodyne single laser TILDAS instrument and find that we can achieve a precision of 5 per meg (standard error) with 12 reference-sample iterations. The gas can be frozen from the laser sample cell back to the cold finger in <30 seconds and can be repeatedly introduced into the laser chamber without fractionation. We also eliminate the CO_2-N_2 gas mixing step (~30 minutes) because N_2O and CO_2 are both frozen into a ½" diameter silica cold finger and warmed in the small volume. Admittance into the laser chamber then results in instantaneous complete mixing. We are currently testing the precision of this technique for CO_2 gases with a wide range of oxygen isotope compositions, and evaluating the ultimate precision that can be achieved with multiple sample-standard comparisons.