



## **Comparison of fragment technique with MAT 253 ULTRA and O<sub>2</sub>-CO<sub>2</sub> exchange method for measuring triple isotope composition of CO<sub>2</sub>**

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Anomaly in oxygen isotopes in CO<sub>2</sub>, also called <sup>17</sup>O-excess is an important tracer to study CO<sub>2</sub> exchange between atmosphere and biosphere. With Isotope ratio mass spectrometers (IRMS) it is impossible to measure  $\delta^{17}\text{O}$  of CO<sub>2</sub> directly due to interference from mass 45. With the newly developed high-resolution mass spectrometer, it is possible to measure  $\delta^{17}\text{O}$  in O<sub>2</sub> fragments formed from CO<sub>2</sub> inside the mass spectrometer ion source. The fragment measurement is only possible with a mass resolution better than  $\sim 4700$  which is achievable with modern high resolution stable isotope ratio mass spectrometer such as MAT 253 ULTRA.

Here we compared CO<sub>2</sub>-O<sub>2</sub> isotope exchange method with a newly developed fragment technique using MAT 253 ULTRA for triple oxygen isotope measurement of CO<sub>2</sub>. CO<sub>2</sub>-O<sub>2</sub> exchange method enables to obtain the  $\delta^{17}\text{O}$  of CO<sub>2</sub> by measuring on O<sub>2</sub> while the fragment method allows to measure  $\delta^{17}\text{O}$  of CO<sub>2</sub> directly from the CO<sub>2</sub> fragment. Enriched CO<sub>2</sub> and normal CO<sub>2</sub> samples are used to compare the two methods. The two techniques require pure CO<sub>2</sub>.

The exchange method is more precise and requires small amount of sample relative to the fragment technique. The main advantage of fragment method is that it is simple and does not require any additional steps and/or chemicals to measure the  $\delta^{17}\text{O}$  value of CO<sub>2</sub> unlike CO<sub>2</sub>-O<sub>2</sub> exchange and fluorination technique. However, the mas signals for isotopes of fragments are relatively small and needs long measurements for a better statistical analysis.