INV-06

Session 5b) Novel Methodology 2: Technical Development

Recent Progress in Isotope Ratio Laser Spectroscopy (IRLS) of Clumped CO_2 and of $\Delta^{17}O$ in CO_2

*Scott Herndon[1], Barry McManus[1], Rick Wehr[1], Christoph Dyroff[1], & David Nelson[1]**

[1] Aerodyne Research, Billerica, United States

*Presenting Author Email: ddn@aerodyne.com

Isotope Ratio Laser Spectroscopy (IRLS) is a powerful technique for the isotopic analysis of materials which exist as or can be converted to small, infrared-active gas phase molecules. IRLS has been applied to carbon dioxide, water vapor, methane and nitrous oxide with excellent results and often providing isotopic variables that are otherwise elusive. In this presentation, we focus on recent advances in the isotopic analysis of carbon dioxide and discuss promising directions for additional progress. High accuracy measurements of the triple oxygen composition of CO_2 using IRLS have been reported by several groups [1,2]. These measurements are unhindered by the isobar problem that makes direct IRMS measurements of ^{17}O-CO_2 impossible. Similarly, IRLS measurements of clumped CO_2 (Δ_{638} ~ Δ_{47}) have been demonstrated with excellent precision, small sample size and rapid measurement time. Fully automated sample preparation lines enable the measurement of more than 100 carbonate samples per week with precision and accuracy at the 10 ppm level [3]. Promising directions for additional progress include further improvements in measurement precision, extension of clumped CO_2 analysis to additional clumped species, improvements to automated sample handling and preparation systems, better understanding of the underlying causes of and corrections for scale contraction and techniques to take advantage of the non-destructive nature of the IRLS measurement process.

References

[1] Stoltmann, T., Casado, M., Daeron, M., Landais, A., and Kassi, S. (2017) Direct, precise measurements of isotopologue abundance ratios in CO_2 using molecular absorption spectroscopy: Application to $\Delta^{17}O$. Analytical Chemistry 89, 10129-10132.

[2] Perdue, N., Sharp, Z., Nelson, D., Wehr, R., and Dyroff, C. (2022) A rapid high-precision analytical method for triple oxygen isotope analysis of CO_2 gas using tunable infrared laser direct absorption spectroscopy. Rapid Communications in Mass Spectrometry 36, e9391.

[3] Yanay, N., Wang, Z., Dettman, D.L., Quade, J., Huntington, K.W., Schauer, A.J., Nelson, D.D., McManus, J.B., Thirumalai, K., Sakai, S., and Rebaza Morillo, A. (2022) Rapid and precise measurement of carbonate clumped isotopes using laser spectroscopy. Science Advances 8, eabq0611.