Pushing paleoclimate and petroleum research forward: a perspective on the various applications of (HR-IRMS)

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Abstract
Non-stoichiometric ‘clumping’ of heavy isotopes in methane (CH\textsubscript{4}), nitrogen (N\textsubscript{2}), hydrogen (H\textsubscript{2}), and carbon dioxide (CO\textsubscript{2}) have evolved to become powerful tools to better understand the origin and temperature history of natural gas or rock samples. Combined with classical gas mass spectrometry (δD, δ18O, δ13C, δ34S), clumped isotopes (\Delta\deltaD, \Delta\delta18O, \Delta\delta13C, \Delta\delta34S) offer additional dimensions to forensic source discrimination and the characterization of formation processes. While the thermodynamic usability of classical stable gas composition is limited, clumped isotope equilibrium distributions are solely dependent on formation temperature and it has been widely demonstrated that clumping can be used to determine highly precise carbonate and methane formation temperatures (2, 3).

Introduction
We showcase application examples to illustrate the scientific added value of various clumped isotope measurements and introduce the analytical setup to analyze clumped isotope measurements.

Analytical setup
The analysis of clumped isotopes is done by classical IRMS, such as the Thermo Scientific\textsuperscript{®} 253 Plus\textsuperscript{TM} 10V IRMS, or without a Thermo Scientific\textsuperscript{®} Kiel IV Carbonate Device (Figure 14). Several features, such as a re-designed magnet for better peak shapes, cup shielding for suppressed pressure baseline, Thermoscientific\textsuperscript{®} 10V Amplifier Technology for outstanding signal-to-noise on tiny signals, improved vacuum system for lower backgrounds, inert capillaries to prevent isotope resetting, a background correction of the measured clumped CO\textsubscript{2} and δD values, a three-compartment cooling setup for the CO\textsubscript{2} cell and the N\textsubscript{2} cell, and a computer-controlled purification trap to remove inconsiderable contaminants, and a half-mass detector to enable interference correction, are dedicated to allow for highly precise analysis of δD and δ\textsubscript{13}C (4-6).

The analysis of clumped isotopes in methane, hydrogen, and nitrogen (Figure 16) is done by means of High-Resolution IRMS as Thermo Scientific\textsuperscript{®} Ultra-HR-IRMS4 (Figure 16). These measurements rely on the Ultra-HR-IRMS capability to resolve isotopic interference on the analysis of interest (e.g. δD, δ18O, δ13C, δ34S).

Clumped isotope analyses in various gases are emerging in atmospheric, petroleum research, and beyond. For instance, clumped isotope measurements can be used to discriminate different methane sources. When combined, these 4 tools can make high-precision δ18O, δ34S, δD, δ13C measurements on a 10–100 µg sample.

Conclusions
Clumped isotope analyses in various gases are emerging in many fields of Earth sciences. They have proven to be accurate and precise tools with versatile applications in atmospheric, research, paleoclimate reconstruction, and natural gas science.

References
10. Patrick, J., and J. (2021) Clumped isotope analyses in various gases are emerging in many fields of Earth sciences. They have proven to be accurate and precise tools with applications in atmospheric, research, paleoclimate reconstruction, and natural gas science. (2022) Thermo Fisher Scientific Inc. All rights reserved.

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