Methane clumped isotopologue thermometry of Icelandic geothermal gases

PATRICK BEAUDRY[1*], JEEMIN H. RHIM[1], ANDRI STEFÁNSSON[2], JENS FIEBIG[3] AND SHUHEI ONO[1]

[1]Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, USA (*correspondence: pbeaudry@mit.edu)
[2]Institute for Earth Sciences, University of Iceland, Reykjavík, Iceland
[3]Institut für Geowissenschaften, Goethe-Universität, Frankfurt am Main, Germany

Geothermal fluids and volcanic fumaroles often contain methane (CH_4) and other small hydrocarbons. Those hydrocarbons could be sourced from abiotic processes including Fischer-Tropsch-type synthesis during water-rock reactions or thermochemical breakdown of organic matter, which is ultimately biotic in origin. While the distinction between the isotope signals of these processes may be ambiguous, the temperatures derived from clumped isotope analysis can help us further constrain the origin of methane. We sampled steam vents and geothermal well fluids from Iceland to measure their CH_4 clumped isotopologue compositions. Apparent equilibrium temperatures were calculated based on the thermodynamics of the isotope exchange reaction among the four measured isotopologues of methane ($^{13}CH_3D + {}^{12}CH_4 \leftrightarrow {}^{13}CH_4 + {}^{12}CH_3D$). We compared these temperatures to those derived from conventional $\delta^{13}C_{CO2}$-$\delta^{13}C_{CH4}$ and $\delta D_{H2O(l)}$-δD_{CH4} isotope thermometers, those estimated from silica solubility and those measured directly downhole in the geothemal reservoir and in the fumarole discharges. Our data reveal a generally high-temperature origin for CH_4 (>250°C). However, there are also important differences between the three isotope and isotopologue equilibration temperatures, likely related to their different rates of isotopic re-equilibration and different sources for CO_2 and CH_4. These results show that CH_4 clumped isotope abundances can provide important constraints on CH_4 formation and origin, independent from those of more conventional isotope systems, which may be more easily affected by mixing. The consistently high temperature signal indicates a high temperature origin of methane in Icelandic geothermal gases. We will discuss the potential roles of pyrolysis versus abiotic methane synthesis and their implications.