

Tracing H₂ Loss in the Deep Subsurface with Hydrogen and Clumped Isotopes

TING XU^{1,2}, HAO XIE^{1,2}, XIAOMEI WANG^{3,4}, KUN HE^{3,4},
YONGBO PENG^{2,5}, CHUNLONG YANG^{3,4}, FENGTAI
TONG^{2,5} AND HUIMING BAO^{1,2}

¹International Center for Isotope Effect Research, Nanjing University, China

²Frontiers Science Center for Critical Earth Material Cycling, School of Earth Sciences and Engineering, Nanjing University, China

³Research Institute of Petroleum Exploration & Development, PetroChina, Beijing, China

⁴Key Laboratory of Petroleum Geochemistry, China National Petroleum Corporation, Beijing, China

⁵Nanjing University

Natural hydrogen is a zero-carbon-emission energy source with potential for providing large-scale and inexpensive energy production. Exploration of natural hydrogen have been limited by uncertainty in its formation mechanisms, accumulation preferences, and stability under various conditions. Primary pathways for subsurface hydrogen loss include hydrogenation/oxidation reactions, diffusive leakage through cap rocks, and microbial consumption. Although hydrogen isotope ratio ($\delta^2\text{H}$) could reflect these processes, its utility is often hindered by the variety of confounding factors such as isotopic exchange. In contrast, clumped isotope signature ($\Delta^2\text{H}^2\text{H}$) is independent of isotopic values of external hydrogen-bearing species and thus provides a reliable high-dimensional constraint to these complex processes.

In this study, we explore the utility of clumped isotopes of hydrogen. First, we developed high precision analyses of clumped isotope ($\Delta^2\text{H}^2\text{H}$) measurements on the Thermo Scientific Ultra mass spectrometer. We established analytical accuracy across a wide range in $\delta^2\text{H}$ through equilibration experiments. Second, we conducted theoretical calculations of isotopic effects in the various mechanisms of hydrogen loss. We performed quantum chemical calculations using density functional theory (DFT) to determine kinetic isotope effects (KIEs) for H₂ oxidation by potential oxidants (SO₄²⁻, SO₃²⁻, toluene radical, methyl radical). Building on these, we computed how isotopologue ratios evolve during these kinetic processes. The high-dimensional constraints from $\delta^2\text{H}$ - $\Delta^2\text{H}^2\text{H}$ patterns allow for a clear distinction between hydrogen loss mechanisms and tracing them in nature. Thirdly, we simulated the evolution of isotopic signatures under coupled effects of isotope exchange and oxidation processes by solving the time-dependent equations for isotopologues. Finally, we show some preliminary analyses of H₂ in natural gas samples from the deep reservoirs in Sichuan Basin, China.