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Nanopore Influence on the Geochemical Properties of Water in Earth's Lithosphere

Oliver Plümper[1], Alireza Chogani[1], Helen E. King[1], and Benjamin Tutolo[2]
[1]Utrecht University, Department of Earth Sciences, Utrecht, Netherlands (o.plumper@uu.nl)
[2]University of Calgary, Department of Earth, Energy, and Environment, Calgary, Canada

Water, a principal component of Earth's fluids, interacts with rocks in ways that profoundly influence lithospheric phenomena. These interactions are fundamental to both geochemical and geodynamic processes, extending their impact to areas of societal importance such as subsurface energy extraction and storage, and the formation of vital metal deposits for green energy technology. Additionally, the interplay between fluids and rocks significantly affects the Earth's carbon cycle, influencing atmospheric CO_2 levels, climate, and overall planetary habitability. The traditional perspective suggests that fluids move through the lithosphere without being affected by the unique properties that emerge when matter is confined to the nanoscale. Contradicting this view, our research reveals that rocks involved in a variety of lithospheric processes consistently show nanoporosity, primarily with pores smaller than 100 nanometers. Within these small spaces, water behaves differently than it does in larger environments. Through molecular dynamics simulations, we have quantified water's relative permittivity—a critical factor in its geochemical behavior— when confined in natural nanopores. Our findings demonstrate that, under a wide range of lithospheric conditions, from ambient to extreme temperatures up to 700 °C and pressures up to 5 GPa, water's permittivity within these nanopores significantly deviates from that in its bulk state. Our thermodynamic equilibrium models indicate that this difference markedly reduces mineral solubility and alters ion speciation in natural settings. These pore-size-dependent properties may exert a primary influence on rock reactivity and the evolution of aqueous geochemistry during fluid-rock interactions.