

Charting Hydrogen Pathways: Modeling the Phase Behavior of Hydrogen in Superhot Rock Geothermal Brine

MARWAH ALSINAN^{1,2}, ILENIA BATTIATO¹ AND
ANTHONY KOVSECK¹

¹Stanford University

²Aramco

Superhot rock (SHR) geothermal systems ($T > 374$ °C) represent a promising source of zero-carbon, always-on power, as well as a potential pathway for hydrogen production. Critical knowledge gaps, however, hamper large-scale energy deployment, including limitations of conventional geochemical exploration tools at supercritical conditions, poorly understood chemical processes under extreme temperatures and pressures, and the lack of robust thermodynamic formulations. Understanding and modelling accurately hydrogen/brine phase behavior is vital for overcoming these challenges, optimizing reservoir performance, and for ensuring sustainable operations and environmental safety.

Thermodynamic modeling was employed in this study to investigate high-temperature interactions between water and olivine, with particular emphasis on hydrogen phase behavior at supercritical pressures and temperatures relevant to SHR geothermal systems. Multiple theoretical frameworks were reviewed and implemented, notably the newly proposed thermodynamic equations for hydrogen by Plyasunov and Korzhinskaya (2021), which target crust and upper mantle conditions. The analysis focused on modeling the kinetics and equilibrium of olivine oxidation by aqueous fluids at pressures up to 600 MPa and temperatures up to 1250 °C, exceeding the serpentine stability field, and was validated against experimental data from analogous systems and buffers ([1];[2];[3]).

The results indicate that olivine reacts with water to form Mg-rich olivine, Fe-rich spinel, and silica with accompanying release of molecular hydrogen. This study helps refine thermodynamic models for predicting phase behavior under SHR-relevant conditions, highlighting the most effective formulations parameterized by temperature and pressure. A deeper understanding of these formulations is critical for evaluating SHR working fluid cycles, as well as the chemical and energy potential of this system. By shedding light on the mechanisms of hydrogen generation, this work underscores the need for further research and technological advancements, ultimately supporting the development of SHR geothermal energy as a viable, carbon-free resource capable of meeting long-term energy demands and reducing reliance on fossil fuels.

References:

- [1] Kishima, N., & Sakai, H. (1984). Fugacity-concentration relationship of dilute hydrogen in water at elevated temperature and pressure. *Earth and Planetary Science Letters*, 67(1), 79-86. [https://doi.org/10.1016/0012-821X\(84\)90040-2](https://doi.org/10.1016/0012-821X(84)90040-2).
- [2] Scheuermann, Xing, Ding, & Seyfried. (2020). Experimental measurement of $H_2(aq)$ solubility in hydrothermal fluids: Application to the Piccard hydrothermal field, Mid-Cayman Rise. *Geochimica et Cosmochimica Acta*, 283, 22-39. <https://doi.org/10.1016/j.gca.2020.05.020>.
- [3] Zelenski, M., Plyasunov, A.V., Kamenetsky, V.S. *et al.* (2022). High-temperature water–olivine interaction and hydrogen liberation in the subarc mantle. *Contrib Mineral Petrol*, 47(177). <https://doi.org/10.1007/s00410-022-01910-z>