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Thermodynamic and mass balance constraints on hydrogen production in hydrothermal systems

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Hydrogen is the principal electron donor in anaerobic metabolic reaction that take place in organic matter-starved environments such as bare rock-hosted hydrothermal systems in the oceans. The basic idea is that hydrogen is produced by hydrolysis of ferrous oxide components in rocks, e.g., $Fe_2SiO_4 + H_2O = Fe_2O_3 + SiO_2 + H_2$.

Hydrogen is a prerequisite in potential prebiotic organic synthesis reactions and metabolic pathways that operate independent of photosynthesis products. It has furthermore been suggested that hydrogen supports microbial ecosystems associated with serpentinization, basaltic aquifers, and volcanic-hosted hydrothermal systems. Hence, there is considerable interest from biologists in assessing geological sources of hydrogen and ample opportunity for petrologists to contribute to an interesting debate and a challenging scientific problem.

Geochemical mass balance calculations, using ferric/ferrous ratios of rocks and minerals, have been employed to estimate oxygen fugacities and hydrogen outputs in magmatic-hydrothermal systems. Equilibrium thermodynamic constraints (phase petrology and geochemical reaction path models) can also be used to estimate aqueous hydrogen activities in water-rock reaction systems. Both methods have strengths and weaknesses, and they are sometimes mixed up such that mass balance is mistaken for phase equilibria. This contribution reviews the different approaches and highlights some of the potential advantages and pitfalls. Recent experimental and observational advances in understanding serpentinization reactions and consequences for hydrogen production in peridotite-water reaction systems are also discussed.