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Induced Hydrogen Generation in Basalt–CO_2–Water Interaction: Competition Between Carbonate Mineralization and Early Methanogenesis during CO_2 Storage

TIAGO DE ABREU SIQUEIRA[1], THIERRY MENDES DOS SANTOS[1], ROMMULO VIEIRA CONCEIÇÃO[1], RENAN GUILHERME MARIN[1], MORGANA BAZZAN DESSUY[1], ANDREA JELINEK[1], ANA MARIA MIZISAKI[1], JORGE FERREIRA JR.[2], MARCO THOALDO ROMEIRO[3] AND PEDRO COSTABILE[1]

[1]Universidade Federal do Rio Grande do Sul
[2]UFRGS
[3]PETROBRAS

Basaltic reservoirs are widely promoted as ideal hosts for permanent CO_2 storage through rapid mineral carbonation. Yet, when CO_2 is injected into Fe(II)-rich basalts, carbon does not follow a single pathway. Here we demonstrate that CO_2 storage in basaltic systems is governed by a dynamic competition between redox-driven hydrogen generation, early abiotic methanogenesis, and delayed carbonate mineralization. Hydrothermal batch experiments were conducted at 150 °C and 8–10 MPa CO_2 using high-Ti basalts from the Paraná–Etendeka Large Igneous Province reacted with saline water (solid/fluid ratio 1:5) over 5, 10, and 20 days. Gas evolution (H_2, CH_4), fluid alkalinity, iron redox state, and mineralogical transformations were integrated to resolve electron and carbon fluxes during fluid–rock interaction. Progressive oxidation of Fe(II) to Fe(III), with negligible change in total Fe, confirms sustained redox cycling as the electron source for induced hydrogen generation. However, hydrogen does not accumulate initially. Methane forms rapidly, reaching 151 μmol L^{-1} after 5 days and increasing to 230 μmol L^{-1} by 20 days, whereas free H_2 remains undetectable at early stages and only rises significantly at 20 days (138 μmol L^{-1}). Stoichiometric constraints indicate that methane formation consumes substantially more hydrogen than is measured in the gas phase, demonstrating that CO_2 reduction ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) initially outcompetes both hydrogen accumulation and carbonate precipitation. Simultaneously, fluid alkalinity increases from 96 to >650 mg L^{-1} (as $CaCO_3$ equivalent), reflecting intense silicate dissolution and progressive buffering of the CO_2-rich fluid. Despite thermodynamic favorability, carbonate phases appear only at later stages, indicating kinetic suppression during early redox-dominated regimes. We propose a carbon competition framework in which injected CO_2 is first diverted into reduced gaseous species through methanation, delaying permanent mineral trapping. Only as reactive CO_2 and reducing capacity become progressively limited does carbonate precipitation emerge as the dominant long-term sink. These findings challenge the assumption of monotonic carbon mineralization in basalt-hosted storage and reveal basalt–CO_2 systems as self-evolving redox reactors coupling hydrogen generation with transient carbon reduction. Quantifying this competition is critical for predicting storage efficiency and for designing integrated hydrogen–CCUS strategies in Fe-rich volcanic reservoirs.