# Competing redox reactions for hydrogen oxidation in the aqueous system $CO_2$-$H_2$-$Fe_2O_3$

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The redox reactions involving the oxidation of molecular hydrogen are investigated in a pleothora of (geo)chemical systems – from the interstellar space [1] to hydrothermal systems with abiotic formation of hydrocarbons [2] to underground hydrogen storage sites to different avenues of industrial $CO_2$ utilization [3].

This study is focussing on the competing and perhaps not independent reactions of molecular hydrogen in the simultaneous presence of two oxidants – hematite and carbon dioxide. Gas mixtures of different ratios of argon:$CO_2$:$H_2$ have been reacted with a distinct grain size fraction (100-400 µm) of natural hematite in the presence of aqueous water in gold capsules as reaction cells in high-pressure reactors. The reaction was investigated at a pressure of 20 MPa and temperatures from 333 to 573 K for durations of 1 to 7 days. After the experiments the gases $CO_2$, CO, $H_2$, and the hydrocarbons up to $C_5$ as well as volatile, more oxidized organic compounds have been quantified. The carbon isotopic compositions of $CO_2$ and methane, ethane and propane have been analysed for selected samples. On the solid residues secondary minerals were identified by SEM, EDX and Raman analyses.

The results delineate a regime shift with temperature: At low temperatures a system dominated by oxidation of molecular hydrogen by the iron oxide surface – with concomitant precipitation of siderite crystals on the edges and kinks of the hematite surface and no visible magnetite formation or hydrocarbon formation. And at high temperatures a system whereas hydrocarbons represent a significant percentage of the products of molecular hydrogen oxidation with lower precipitation of siderite, but stable magnetite areas on the bulk hematite grains. Most interesting is the detailed understanding of kinetics in the overlap of both systems in the temperature range of 363 – 453 K, as these conditions represents those encountered in deep geological $CO_2$ storage sites to hydrocarbon reservoirs.

[1] Kumar *et al.* (2018) *Science Advances* **4**, eaar3417. [2] McCollom (2016) *PNAS* **113**, 13965-13970. [3] Schaub (2018) *Phys. Sci. Rev.* **3**, doi:10.1515/psr-2017-0015.