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# Multistage serpentinization and natural $H_2$ generation in ophiolitic ultramafic rocks of the Northern Apennines

**ALESSANDRA MONTANINI**[1], VIVIAN AZOR AZOR DE FREITAS[2], TIZIANO BOSCHETTI[1] AND ISABELLE MORETTI[3]

[1]University of Parma
[2]National Agency of Petroleum, Natural Gas and Biofuels (ANP)
[3]Université de Pau et des Pays de l'Adour

Serpentinization of ultramafic rocks is widely recognized as one of the main processes responsible for generating natural $H_2$. The partially serpentinized peridotites and pyroxenites of the External Ligurian units (Northern Apennines) provide a favorable setting for assessing natural hydrogen systems. We conducted an integrated geological and geochemical investigation to evaluate the potential for subsurface $H_2$ generation and accumulation [1], [2]. The study combined analyses of dissolved gases in spring waters and soil-gas measurements with petrographic, mineralogical, and whole-rock geochemical characterization of ultramafic rocks, redox-state determinations and thermodynamic modelling of spring waters. Several springs contain dissolved $H_2$ at low to moderate concentrations (up to ~100 μM), compared with serpentinized peridotite systems worldwide. A key locality is Mt. Prinzera, where a hyperalkaline spring spatially associated with mantle-derived ultramafic rocks contains detectable dissolved $H_2$. Peridotite, pyroxenite, and serpentinite were geochemically characterized to reconstruct the evolution of serpentinization and to assess their $H_2$-generation potential. The main serpentinization event occurred during Middle–Late Jurassic mantle exhumation and involved extensive replacement of olivine and pyroxenes by serpentine ± magnetite at ~220–300 °C, as constrained by petrography and mineral equilibria. Currently, the redox conditions and the oversaturation with respect to (Fe)-bearing lizardite and magnetite in the most evolved hyperalkaline fluid suggest ongoing fluid–rock interactions associated with $H_2$ generation at Mt. Prinzera under markedly low-temperature conditions, consistent with $CO_2$–$CH_4$ isotopic fractionation related to a bacterial methanogenic environment. $H_2$ is likely produced through oxidation of $Fe^{2+}$ in serpentine and/or magnetite rather than primary silicates, resulting in limited but measurable production. Microbial processes may further regulate hydrogen concentrations through continuous consumption, although the presence of fossil $H_2$ accumulations cannot be ruled out.

[1] Freitas, Montanini, Moretti, Artoni, Segadelli, Izerumugaba, Battani, Etiope (2025). Mar. Pet. Geol., 182, 107594.

[2] Freitas, Boschetti, Montanini, Moretti (2026). Chem. Geol., 704, 123266.