

Hydrogenotrophic metabolisms in the subsurface: insights from natural hydrogen seeps in diverse geological settings

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Hydrogen is a fundamental electron donor in several microbial metabolisms and is considered to be the main energy currency of microbial communities in anaerobic environments. Hydrogen, both naturally released and produced industrially via water hydrolysis, represents one of the keys to a greener energy society. Known geological hydrogen emissions are widespread and are mainly associated with hydrothermal systems at plate margins or to radiolysis of water in stable cratons. In geological settings, hydrogen can be naturally produced by a variety of processes, including microbial fermentation of organic matter, radiolysis of water, and hydration of iron-rich ultramafic rocks. When hydrogen is released from depth, it travels towards the surface, traversing a large subsurface ecosystem. Microbial communities in the subsurface can use hydrogen as an energy source, coupling its oxidation to the reduction of a variety of different compounds, through a diverse group of enzymes called hydrogenases, catalyzing the oxidation of molecular hydrogen to protons and electrons. These diverse enzymes use tangled organometal complexes built around a binuclear Ni-Fe, Fe-Fe or Fe center, with bound CO and CN(-) groups, as well as multiple FeS centers. Understanding the diversity of hydrogenases in the

subsurface and the role of trace elements' availability in controlling their spatial distribution is crucial to quantify the subsurface microbial utilization of molecular hydrogen derived from geological reactions. Here, we will present data on the diversity of hydrogenases from a number of deeply-sourced springs located in diverse convergent and divergent margins worldwide. The results will help to establish the baseline of hydrogenotrophic metabolisms in the subsurface, complementing our knowledge of the microbial influence on hydrogen cycling in various geological settings. Data such as these will improve our understanding of subsurface hydrogen aiding both natural hydrogen exploration and geological hydrogen storage.