Native H2 generation & consumption through abiotic reactions: mineral catalysis and formation of short-chain organic compounds in the Marianna Trench

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The only known active serpentinite-hosting mud volcanoes on Earth are located in the Marianna forearc subduction zone. They were drilled during IODP Expedition 366 (Dec. 2016 - Feb. 2017). Mud, water and gas samples from Asùt Tesoru seamount have been analyzed for their mineralogical, chemical and isotopic compositions. The reduction of water by ferrous iron produces hyperalkaline pore fluids (pH 12.5) rich in dissolved H_2 (up to 2 mM), prone to react with accompanying DIC (up to 4.5 mM). Petrographic observations of the mud reveal elevated amounts of Cr-rich oxides that may have favored Fe^{2+} oxidation and H_2 generation, as suggested by the large amounts of magnetites nucleated on their surface. Furthermore, polymetallic sulfides (Ni, Co, Zn and Cu-rich) may have in turn catalyzed Fischer-Tropsch-Type (FTT) reactions, consuming both H_2 and CO_2 to form organic matter.
This H_2-rich environment provides conditions that produce carbon species like volatile fatty acids (VFAs), short-chain alcohols, and light hydrocarbons. Ionic chromatography and 1H NMR measurements show they are mostly composed of formate and acetate (up to 100 and 40 µM), associated with methanol (up to 30 µM). The gas phase of the serpentine mud is composed of H_2 and CH_4 (up to 95%). The $\delta^{13}C$ values of methane are as heavy as -16 ‰, in good agreement with reported abiogenic values. In addition, measured ^3He concentration and $^3He/CO_2$ ratios suggest a mantle-derived inorganic carbon source, without excluding the possibility of a reaction with subducted sedimentary organic matter. The fractionation factors between δD of CH_4 and H_2O, and $\delta^{13}C$ of CH_4 and CO_2 were also measured, and suggest equilibrium temperatures (and potential formation temperatures) greater than 300°C.
These data point to H_2 generation at depth and a subsequent consumption during its ascent, leading to the abiotic formation of low molecular weight organic compounds in the Marianna's mud volcanoes. Such observations not only bring new constraints on the reaction pathways leading to the formation of precursor molecules essential to life in serpentinizing environments, it could also shed new light on native H_2 budget in similar, iron and CO2-rich, terrestrial environments.

Mots-Clés : native H2, subduction zone, Fischer-Tropsch-Type reactions, catalysts, mud volcanoes

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