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Heterogeneous magnetite nucleation in fluid inclusions as driving force for olivine oxidation coupled with hydrogen production at high pressure

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We studied the crystallisation evolution of magnetite-bearing multiphase inclusions hosted in metamorphic olivine of harzburgites from the Cerro de Almirez (Betic Cordillera, Spain), which have been interpreted as final products of the trapping of the aqueous fluid produced by the subduction-zone dehydration of former serpentinites. The chemical exchange between inclusion fluid and olivine started soon after entrapment, at peak P-T conditions of 1.6-1.9 GPa and 650-700 °C, and continued during cooling along the retrograde path, with the coexistence of olivine and magnetite with orthopyroxene, chlorite, talc, antigorite and the destabilisation of olivine and antigorite into brucite and low-temperature chrysotile serpentine, as recognised by Raman analyses. Thermodynamic modelling and mass balance calculations demonstrate that pure water trapped in inclusions in metamorphic olivine is expected to trigger the oxidation of the fayalite component of olivine, producing a mineral assemblage made of magnetite and orthopyroxene and producing molecular hydrogen, where the elemental redox processes are Fe^{2+} of olivine that oxidises to Fe^{3+} and H_2O that reduces to H_2. Probable H_2 trapped in the olivine host close to the inclusion wall has been detected by Raman spectroscopy. To corroborate its presence, we performed quantitative mass spectrometry analyses of the fluid phase trapped in the multiphase inclusions and of the olivine crystals hosting the inclusions, revealing that 1 kilogram of olivine matrix contains 6.2 ± 0.1 mmol of H_2. We identify two synergistic driving forces of the whole process, which has the peculiarity to produce molecular hydrogen at apparently oxidising conditions: i) the building up of an epitaxial interface between olivine and magnetite, and ii) the olivine ability to act as a trap for H_2 at high pressure. The olivine + H_2O system of these natural microreactors simulates a process of oxidation of the mantle by water, with production of H_2 at fO_2 conditions (FMQ+2) at which water cannot be dissociated.