Diamond formation by carbon saturation in C-O-H fluids at Lago di Cignana UHPM unit (western Alps, Italy)

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Microdiamonds in garnet of graphite-free ultrahigh pressure metamorphic (UHPM) rocks from Lago di Cignana (western Alps, Italy) represent the first occurrence of diamond in a low-temperature subduction complex of oceanic origin (T = 600°C; $P \geq 3.2$ GPa). The presence of diamonds in fluid inclusions provides evidence for carbon transport and precipitation in an oxidized H_2O-rich C-O-H crustal fluid buffered by mineral equilibria at sub-arc mantle depths. The structural state of carbon in fluid-precipitated diamonds was analyzed with 514 nm excitation source confocal Raman microspectroscopy. The first order peak of sp^3-bonded carbon in crystalline diamonds lies at 1331 (±2) cm^{-1}, similar to diamonds in other UHPM terranes. The analysis of the spectra shows additional Raman features due to sp^2 carbon phases indicating the presence of both hydrogenated carbon (assigned to trans-polyacetylene segments) in grain boundaries, and graphite-like amorphous carbon in the bulk, i.e. showing a structural disorder much greater than that found in graphite of other UHPM rocks. In one rock sample, defective microdiamonds are recognized inside fluid inclusions by the presence of a weaker and broader Raman band downshifted from 1332 to 1328 cm^{-1}. The association of sp^3- with sp^2-bonded carbon indicates variable kinetics during diamond precipitation. We suggest that precipitation of disordered sp^2-bonded carbon acted as a precursor for diamond formation outside the thermodynamic stability field of crystalline graphite. Diamond formation started when the H_2O-rich fluid reached the excess concentration of C required for the spontaneous nucleation of diamond. The interplay of rock buffered f_{O_2} and the prograde P-T path at high pressures controlled carbon saturation (a_C=1) in the fluid phase. Thermodynamic modeling confirms that the C-O-H fluids from which diamond precipitated must have been water-rich ($0.992 < X_{H2O} < 0.997$), assuming that f_{O_2} is fixed by the EMOD equilibrium.