

## 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 ( $T = 600^{\circ}\text{C}$ ;  $P \geq 3.2$  GPa). The presence of diamonds in fluid inclusions provides evidence for carbon transport and precipitation in an oxidized  $\text{H}_2\text{O}$ -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  $\text{sp}^3$ -bonded carbon in crystalline diamonds lies at  $1331 (\pm 2) \text{ cm}^{-1}$ , similar to diamonds in other UHPM terranes. The analysis of the spectra shows additional Raman features due to  $\text{sp}^2$  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  $1328 \text{ cm}^{-1}$ . The association of  $\text{sp}^3$ - with  $\text{sp}^2$ -bonded carbon indicates variable kinetics during diamond precipitation. We suggest that precipitation of disordered  $\text{sp}^2$ -bonded carbon acted as a precursor for diamond formation outside the thermodynamic stability field of crystalline graphite. Diamond formation started when the  $\text{H}_2\text{O}$ -rich fluid reached the excess concentration of C required for the spontaneous nucleation of diamond. The interplay of rock buffered  $f_{\text{O}_2}$  and the prograde  $P$ - $T$  path at high pressures controlled carbon saturation ( $a_{\text{C}}=1$ ) in the fluid phase. Thermodynamic modeling confirms that the C-O-H fluids from which diamond precipitated must have been water-rich ( $0.992 < X_{\text{H}_2\text{O}} < 0.997$ ), assuming that  $f_{\text{O}_2}$  is fixed by the EMOD equilibrium.