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Graphitic carbon formation through calcite reduction in blueschist metasediments from Alpine Corsica (France)

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The geochemistry of reduced carbon in subduction zones is strongly affected by mineral equilibria. We study here the geochemistry of carbon in siliceous-marbles at the direct contact with serpentinites in the Alpine eclogitic meta-ophiolithic units of northern Corsica (France). We have combined petrology, Raman spectroscopy and carbon isotopy to provide a description of both the organic and carbonate components of the rocks across a reaction front where the reaction $CaCO_3+SiO_2+2H2=CaSiO_3+C+2H_2O$ is evidenced.

The continuous reaction zone is composed by a centimeter thick pale nephrite layer at the contact with the serpentinites, followed by a thin wollastonite layer and a 5 to 20 cm thick dark zone composed of wollastonite, carbonaceous material (CM), quartz but no carbonates. There is a sharp transition to the overlying original metasediment composed of calcite+quartz which is significantly less rich in CM. Raman spectroscopy shows that CM is much more graphitic in the reaction zone than in the original sediment. Significant isotopic differences are observed apart the reaction front with δ13C (CM) and δ13C (calcite) around -15‰ and 1.3‰ respectively in the original rock far from the reaction zone, whereas δ13C (CM) is around -1‰ in the reaction zone.

We interpret the graphitic CM in the reaction zone as formed from the destabilization and reduction of calcite due to the diffusion of reducing fluids from the underlying serpentinite unit. Mass balance calculations support this hypothesis and show that a complete reduction of carbonates might have occurred. The timing of this abiotic macromolecular and graphitic C formation is discussed. We show that the combined study of isotopic geochemistry and structure of inorganic and organic carbon in metamorphic rocks might be suited to reveal with great fidelity redox gradients in subduction zones.