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Subduction Metamorphism of Ophicarbonates beyond the Stability of Antigorite: insights into Carbonate Dissolution vs. Decarbonation from the Almirez ultramafic massif (S. Spain)

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Subduction zone processes play a key role in determining the time and length-scales of long-term element cycles like the deep carbon cycle. Recent improvements in thermodynamic modelling of fluid properties at high pressure and new experiments have underlined the importance of carbonate dissolution by subduction fluids from dehydration reactions for the transfer of carbon out of the subducting slab. However, natural case studies are scarce, in particular regarding the impact of fluids generated by serpentinite dehydration, which are considered as a major dissolution agent for carbon due to the high temperature of antigorite breakdown (about 650°C) and the potentially large volumes of hydrated peridotites occurring in the upper part of the subducting oceanic mantle lithosphere. Here we report the occurrence of meta-ophicarbonate lenses within prograde Chl-harzburgites in the Almirez ultramafic massif (Betic Cordillera, S. Spain). The presence of these lenses indicates that carbonate minerals were preserved beyond the stability conditions of antigorite and were not dissolved by deserpentinization fluids. The largest meta-ophicarbonate lens in the Almirez Chl-harzburgites measures 8 x 160 m and is composed of a high-grade assemblage of olivine, Ti-clinohumite, diopside, chlorite, dolomite, calcite and Cr-bearing magnetite with a granofelsic to banded appearance. In this assemblage we identified, for the first time in the Betic Cordillera, aragonite inclusions in olivine and diopside using coupled EBSD and chemical mapping. Calcite-dolomite thermometry and thermodynamic equilibrium modelling constrain the peak metamorphic conditions to 1.7 – 1.9 GPa and 680 °C at very low XCO_2. These conditions compare well with P-T-estimates for the surrounding Chl-harzburgites. There is strong evidence that the protolith of the carbonate rocks within Chl-harzburgites was an ophicarbonate zone: bulk rock contents of Ni and Cr are similarly high in the carbonate rocks as in Atg-serpentinites and Chl-harzburgites of the Almirez massif, and their major element compositions plot on the $CaCO_3$-antigorite mixing line. As the meta-ophicarbonates are enclosed within prograde Chl-harzburgites, they have experienced a high fluid flux triggered by the antigorite breakdown in surrounding serpentinites at about 660 °C, with a high potential to dissolve carbonates. However, these carbonate lenses retain high amounts of dolomite and calcite (40 – 45 vol%), and their phase assemblages and stable isotope compositions of carbonate (δ18O = 13-17 ‰ V-SMOW and δ13C = -0.5-1 ‰ V-PDB) do not indicate a major fluid-induced decarbonation. The survival of carbonate may be due to the fact that antigorite dehydration occurred at up to 50 – 70 °C lower temperatures in the presence of $CaCO_3$ than in pure serpentinites. This could lead to the formation of a relatively impermeable shell of carbonate-bearing olivine-diopside fels around the meta-ophicarbonates prior to the main serpentinite dehydration, thus protecting the carbonate-richer assemblages from dissolution. The example of the meta-ophicarbonates at Almirez suggests that this mechanism may lead to recycling of substantial amounts of carbon into the deep mantle via subduction of carbonate-bearing serpentinites.

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