Dissolving dolomite in a stable UHP mineral assemblage: Evidence from Cal-Dol marbles of the Dora-Maira Massif (Italian Western Alps)

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ABSTRACT

In deep and cold subduction such as that experienced by the UHP Units of the Western Alps, carbon dissolution is a relevant mechanism for carbon transfer from the slab into the mantle. The UHP impure Cal-Dol-marbles from the Dora-Maira Massif are studied to investigate the poorly known evolution of dolomite during deep subduction. Dolomite shows four stages of growth, from pre-Alpine to early-retrograde Alpine, coupled with chemical variations and distinct included mineral assemblages. To explain the evidence for growth and partial reabsorption of dolomite through HP prograde, UHP peak, and UHP early-retrograde Alpine metamorphism, a chemically simple marble (Cal, Dol, Di, Fo, and retrograde Atg, Tr, Mg-Chl) has been studied in detail. Microstructural relationships, coupled with mineral chemistry, indicate the growth of the assemblage dolomite+diopside+forsterite+aragonite during HP prograde, UHP peak, and UHP early-retrograde evolution.

Mixed-volatile P-T projection modeled in the simple CaO-(FeO)-MgO-SiO2-H2O-CO2 system and T-P-Xco2 petrogenetic grids and pseudosections predict the prograde (1.7 GPa, 560 °C) growth of dolomite in equilibrium with diopside and forsterite through the breakdown of antigorite+aragonite. In a H2O-CO2-saturated system, the subsequent HP-UHP evolution is predicted in the Di+Fo+Dol+Arg stability field in equilibrium with a dominantly aqueous COH fluid [0.0003 < Xco2 < 0.0008], whose composition is internally buffered by the equilibrium assemblage. Thermodynamic modeling indicates that neither the consumption nor the growth of new dolomite generations at UHP conditions can have been induced by metamorphic reactions. The abundant primary H2O+Cal+Dol+Cl-rich Tr+Cl-rich Tlc±chloride fluid inclusions present in UHP Cpx indicate that a dominantly aqueous, saline (salinity >26.3 wt% of NaCl) COH fluid, containing Ca, Mg, and Si as dissolved cations was present during the growth of the UHP assemblage Dol+Cpx+Ol+Arg.

The complex zoning of dolomite is therefore interpreted as due to protracted episodes of dissolution and precipitation in saline aqueous fluids at HP/UHP conditions. Kinetics of dolomite dissolution in aqueous fluids is poorly known, and experimental and thermodynamic data under HP conditions are still lacking. Data on calcite indicate that dissolution at HP is enhanced by a prograde increase in both P and T, by high salinity in aqueous fluids, and/or low-pH conditions. In the studied marble, the P-T path and the occurrence of free high-saline fluids represent favorable conditions: (1) for the inferred dissolution-precipitation processes of the stable dolomite in a closed system, and (2) for possible migration of the dissolved carbonate, if the system would have been open during subduction.

Keywords: Subduction, zoned dolomite, cathodoluminescence, micro-Raman spectroscopy, thermodynamic modeling, COH fluid, dissolution-precipitation, Invited Centennial article

Introduction

In the long-term global carbon cycle, the flux of carbon released in the Earth’s interior by subduction is directly connected with that released from volcanic arcs and, ultimately, can contribute to climate variability. The still poorly constrained nature and composition of the COH fluids generated during deep (i.e., at ultrahigh-pressure conditions) subduction, such as their fate in the Earth’s interior, are responsible for the highly controversial estimations of carbon fluxes to the exosphere (e.g., Kelemen and Manning 2015). In this context, metamorphic evolution of carbonates during subduction plays an important role, because they are relevant constituents of the altered oceanic crust and of the sedimentary materials in convergent settings.

Thermodynamic modeling on natural samples and experi-