

Phase diagrams for $\text{CaCO}_3 + \text{H}_2\text{O}$ and their bearing on the genesis of carbonate melts

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Phase transformations in the system CaCO_3 and $\text{CaCO}_3 + \text{H}_2\text{O}$ have been of primary concern for Earth scientists since early XIX century. Sir J. Hall performed the first investigations in this system in 1798 and pursued various attempts at defining de-carbonation reactions and melting of calcite with water in externally heated gun barrels, successfully performing the first high pressure experiments in geoscience.

Despite two centuries passed, experimental results on phase transformations in CaCO_3 are still contradictory. Discrepancy between ex-situ and in-situ determination of the reaction calcite = aragonite is in the order of 3 GPa at 1200 °C. Experimental data on melting of calcite with an aqueous fluid differ by 300 °C. Uncertainties on the phase diagram for CaCO_3 and $\text{CaCO}_3 + \text{H}_2\text{O}$ have profound consequences in predicting the fate of altered oceanic crust and of metasedimentary materials re-introduced in the mantle at subduction zones.

Multianvil experiments were performed at 4.2 GPa on model bulk compositions in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$, obtained from natural calcite, Al(OH)_3 and silica. Stoichiometric proportions are intended to produce at run conditions kyanite + CaCO_3 + a fluid or/and a melt. Al_2SiO_5 saturation prevents the formation of portlandite and offers a basis for modelling melting of impure marbles. Furthermore the usage of Al(OH)_3 in the starting material allows an accurate control of H_2O added, fixed at 10 wt% in the present study. This amount is expected to produce H_2O -undersaturated melts, on the basis of solubility data determined at low pressure.

Aragonite + kyanite + fluid, and minor lawsonite form at 700 °C, replaced by zoisite at 800 °. At 850 ° and 900 ° a complex sequence of quenching textural features is observed; "chains" and dendrites of CaCO_3 grow nucleating from liquid-solid interface; they are followed by growth of Si-Al-bearing fibres; finally spheres of silica precipitate from the residual fluid exsolved from the liquid carbonate phase. Excess silica is required to prevent the formation of corundum.

Estimates of liquid ? solid proportions, retrieved by image analysis, at known bulk H_2O content, along with the solid ? pore volume proportions in the liquid region of the run charge provide constraints for H_2O solubility in CaCO_3 liquid. Chemographic analysis support the occurrence of a single hydrous silicate carbonate liquid at large $\text{CaCO}_3\text{:H}_2\text{O}$ ratios.

The model system investigated here, and the minimum temperatures of melting found, represent the upper bound of the formation of hydrous Ca-carbonate melts able to metasomatise the mantle at subduction zone environments. Alkali may further promote the generation of Ca-carbonate liquids at lower temperatures.

Keywords: calcite, mixed fluids, carbonate liquids, subduction