



## **CaCO<sub>3</sub>-MgCO<sub>3</sub>-FeCO<sub>3</sub> phase diagram at upper mantle P,T conditions**

E. Franzolin, M.W. Schmidt

Institute of Mineralogy and Petrology, ETHZ, Zurich, Switzerland

At convergent boundaries, volatile compounds are transported in the interior of the Earth affecting the chemical evolution of our planet. H<sub>2</sub>O and CO<sub>2</sub> are the most important compounds affecting phase stabilities during subduction. The stability of carbonates at high pressure is proved by the occurrence of coesite and diamond inclusions in dolomite and magnesite from carbonate-bearing eclogite, with the general succession of carbonates with pressure being calcite – dolomite – magnesite. The fate of carbonates, is controlling the residence time of C in the mantle, affecting its global geochemical cycle and contributing to the chemical and, in carbonate rich sediments, also mechanical structure of subducted crust. Nevertheless the phase diagram of CaCO<sub>3</sub>-MgCO<sub>3</sub>-FeCO<sub>3</sub> is unknown at high pressure and is starting to be investigated to 6 GPa and 1300 °C. Starting materials are natural MgCO<sub>3</sub>, synthetic CaCO<sub>3</sub> and FeCO<sub>3</sub> in different proportions. First experiments have been carried out at 3.5 GPa and temperature between 900 °C and 1100 °C, in Pt-C capsules to fix oxygen fugacity roughly to GCO, thus avoiding siderite oxidation. Runs performed at 900 °C show a miscibility field between CaCO<sub>3</sub> and slightly Ca enriched ankerite (Ca<sub>1.16</sub>Fe<sub>0.84</sub>(CO<sub>3</sub>)<sub>2</sub>). These results are in good agreement with the observation of (Mg,Fe)-calcites with high Mg+Fe contents in experiments on natural bulk compositions. Between the joint dolomite-Ca enriched ankerite and the continuous solid solution siderite-magnesite exists a broad miscibility gap; no three phase field, observed at lower pressure, has been noted. The already known solvus between dolomite and calcite has been constrained. In the ternary diagram, Fe diminishes the width of this 2 phase field until it closes at an X<sub>Mg</sub> near 0.7. As expected, this solvus is narrower at higher temperature (1000 °C and 1100 °C); already at 1000 °C the solvus between calcite and siderite vanishes. A

thermodynamic model (General Point Approximation Model) has been proposed to describe order and unmixing of the system. Future synchrotron X-ray diffraction will determine in-situ the state of disorder of carbonates and the  $R\bar{3} \Leftrightarrow R\bar{3}C$  transition, necessary to improve the thermodynamic model. Selected runs have been observed with TEM and microraman to investigate disordering and reordering after quench. Further experiments at different P-T conditions in multi anvil apparatus are necessary to obtain a full set of thermodynamic properties and a full fledged solid solution model as a function of pressure and temperature.