ESRF	**Experiment title:** Structure mechanisms and transient states related to polymorphic transformations in calcium carbonate at 50 GPa and 2000 K	**Experiment number**:
Beamline:	**Date of experiment**: from: 13/07/2011 to: 16/07/2011	**Date of report**:
Shifts: 9	**Local contact(s)**: Dr. Wilson A. Crichton and Dr. Michael Hanfland	*Received at ESRF:*

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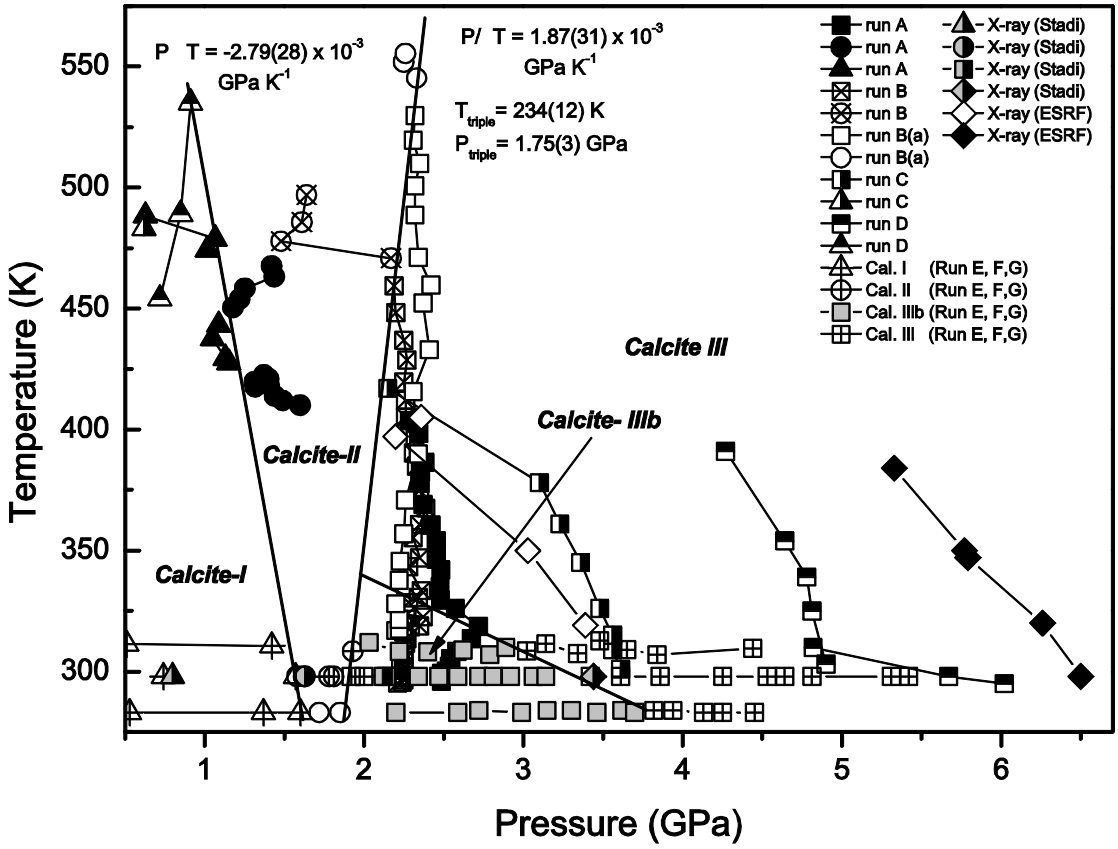
Report:

Calcite, ($CaCO_3$), the predominant inorganic host phase within the global carbon cycle, is exposed to raising pressure and temperature conditions, considering the transport into the depth of the Earth related to subduction processes. This involves a series of polymorphic structural transformations, which are relevant to the conditions following the respective Earth's geotherm. Most recent experimental results suggest the high-pressure structures of so-called calcite-III, calcite-VI and the supposedly metastable calcite-IIIb. Within the scope of the proposed study we attempted complementary information on the crystallographic instability criteria of the calcite-III structure in relation to the existing boundaries towards calcite-II at low pressures and aragonite at high pressure.

Following this intention we collected several sets of single-crystal X-ray diffraction data of $CaCO_3$ loaded into a diamond-anvil cell and applying the composite-gasket heating technique. The technique was chosen in order to provide a stable and uniform temperature conditions across the samples similar to successful experiments under laboratory conditions. A distinct disadvantage of the techniques with small gradients in P and T on the sample and reference materials is the limited mechanical stability of the gasket, which results in limitations of the range of accessible P,T conditions. Accordingly, all experiments carried out within the given beamtime finally were carried out at significantly lower conditions than originally intended in the proposal. Nevertheless, the collected data provide valuable

information with respect to the stability conditions on the boundary to calcite-II, and contributed to the puzzle of the dimorphism involving the phases III and IIIb.

Within the scope of this experiment we were able to collect 11 data points by recording full data sets within the accessible range of reciprocal space. For most of the data sets a full structure refinement was possible after extensive and careful data treatment and applying adequate corrections. The structure variations are small and the evolution of stereochemical parameters does not provide any indication of a significant instability on temperature variation within the given range. The extracted lattice parameters were used to attempt fits to a thermal equation of state which results for second-order BM-EoS type in the values: V_0 = 569.6(1.4) Å^3, K_{T0} = 87.5(5.1) GPa, $(\delta K_T/\delta T)_P$ = -0.21(0.23) GPa K^{-1}, α_0 = 0.8(21.4) x10^{-5} K^{-1} and α_1 10.0(337.0) x10^{-8} K^{-1} for the calcite-III phase. The XRD data allowed cleary to distinguish between four polymorphs occurring within the experimentally achieved P,T range, and together with complementary Raman measurments carried out after the findings of the synchrotron experiment, the phase boundaries of the I-II and II-III transition could be revised and the dP/dT slopes could be bracketed to -2.79(28)x10^{-3} and +1.87(31)x10^{-3} GPa K^{-1}. Moreover, the experimental data suggestthat the so-clled phase IIIb might be a stable phase, as careful Raman investigations provided a reproducebale transition point at approximately 3.2 GPa. The findings are currently merged into a manuscript with the title *The calcite-III puzzle: Pathway of single-crystal transitions*, which is supposed to be submitted by the end of March 2014.



Stability field of the calcite I-II-IIIb-III polymorphs as a function of pressure and temperature. The data is merged from the synchrotron results and complementary Raman spectroscopic measurments using the composite-gasket technique.