IRREGULAR COMPRESSION BEHAVIOUR OF SOLID CO_2 - A VOLUMETRIC AND ULTRASONIC STUDY AT -75°C

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Carbon dioxide is the most abundant volatiles of the Earth beside H_2O and of fundamental relevance in rock forming processes. A re-appraisal of the melting curve of CO_2 and the determination of the stability boundary of silver oxalate ($Ag_2C_2O_2$) by MIRWALD & SCHOTTENBERGER (2004) suggested anomalous changes in dP/dT-slope at 400, 1200 and 2500 MPa. In addition, isothermal runs within the liquid and solid phase field (at 225°, 140° and 13°C) insinuated anomalous compression behaviour at similar pressures. This raised the question whether these anomalies may occur independently of the state of matter and thus may become also relevant for rock-forming processes under fluid conditions. Volumetric pressure experiments on “dry ice” (0.5 cm^3) were undertaken in a piston cylinder vessel (bore: 8 mm) at -75° C. The piston displacement was monitored by two transducers (resolution: ± $0,5*10^{-6}$m). Simultaneously, ultrasonic (us) measurements were performed (through-transmission, probe 150 MHz, 250V), that rely on the determination of the relative time shift of the zero-crossing positions of the wave train. Figure 1 shows the relative compressibility of solid CO_2 revealing three anomalies. No pressure hysteresis is observed. Structurally the cubic structure of CO_2 seems only slightly affected by these volume effects, thus no phase transition is triggered (LIU, 1983). The volumetric data are fully supported by the us-measurements. Generally, these irregular changes in the compressibility of solid and liquid CO_2 may potentially be related to not uniform changes in the intermolecular interaction of the CO_2 molecule at high pressure.

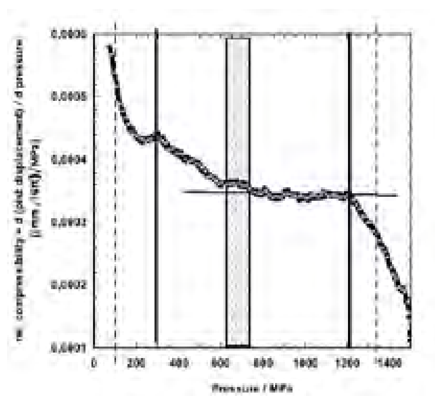

Figure 1: Relative compressibility of solid CO_2 indicating three anomalies at 300, 600-750 and 1200 MPa at -75°C. The two dashed lines at 100 and 1350 MPa confine the pressure ranges where the stress–strain behaviour of the vessel is not steady at compression and decompression.

MIRWALD, P.W., SCHOTTENBERGER, H. (2009): Mitt. Österr. Miner. Ges., 155, 105.
LIU, L. (1983): Nature, 303, 508