CO$_2$ melting and decarbonation reactions at high P-T conditions as indicators for anomalous PVT behaviour of CO$_2$

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A number of dehydrations studies recently revealed a system of PVT anomalies of H$_2$O (Mirwald 2006) the most important fluid component in petrological processes. A similar strategy may be applied to explore the PVT behaviour of CO$_2$, a further important fluid component. First information on anomalous PVT behaviour of fluid CO$_2$ may be gained from the inspection of the available PVT data of CO$_2$ C by Tsiklis et al. (1971) and Shmunov & Shmuloich (1974) which cover the temperature range 100–800°C up to 0.8 GPa. Here, the second derivative of volume vs. pressure reveals a minimum of d^{2}V/dP^2 in the range of 0.5 GPa. First piloting studies on the decarbonation of otavite (CdCO$_3$) (Mirwald, 2004), silver oxalate (Ag$_2$C$_2$O$_4$) and on the melting curve of CO$_2$ (Mirwald, 2005a) have been reported previously. The experiments have now been extended up to the pressure range of 3 GPa .

All experiments were performed with a piston cylinder apparatus using a conventional NaCl cell set up. 50–100 mg of Ag$_2$C$_2$O$_4$ sealed gold capsules served as starting material. While the decarbonation reaction Ag$_2$C$_2$O$_4$ = Ag$_2$ + CO$_2$ could directly be measured, the melting measurements had to be performed on the decomposed product. The reactions were monitored by DPA-technique (Mirwald & Massonne, 1982; Mirwald, 2005b).

The CO$_2$ melting curve re-examined up to 3.5 GPa seems to confirm previous determinations (Tammann, 1912; Bridgman, 1914; Grace & Kennedy, 1967). However, a closer inspection of the data suggests a fine structure of the melting curve in form of slight kinks at 0.5, 1.3 and 2.3 GPa which indicate a sort of triple point topology insinuating a boundary related to a property change in liquid CO$_2$. This hypothesis was cross checked by the determination of the decomposition boundary of Ag$_2$C$_2$O$_4$ which is located about 200K above the CO$_2$ melting curve. The decarbonation data reveal, in accord to the CO$_2$ melting curve, two pronounced inflections at 0.5 and 1.3 GPa. Into this picture fits the recently studied decarbonation boundary of CdCO$_3$ (Otavite) which covers the temperature range between 350–1000°C (Mirwald, 2004). It shows similar inflection characteristics as the silver oxalate decomposition boundary at 0.5 and 1.3 GPa.

Comparison with literature data supports the own findings. In addition to the indication of anomalous PV T behaviour of CO$_2$ at 0.5 GPa (Tsiklis et al., 1971, Shmunov & Shmulovich, 1974) also the decarbonation boundary of FeCO$_3$ up to 1.1 GPa (Weidner, 1972) exhibits an inflection at 0.5 GPa. The inflections at 0.5 and 1.3 GPa of the otavite

decomposition boundary are again in striking accord with the inflections of the other investigated boundaries. Further support for the hypothesis of a PVT anomalies of CO_2 may be gained from the P-T-stability boundary of dolomite (Goldsmith, 1982) which is located in the temperature range of 800 to 1400°C. The decomposition boundary $(CaMg(CO_3)_2 = MgO + CO_2 + CaCO_3$ determined up to a pressure of 1.5 GPa shows two inflections at 0.4 and 1.2 GPa.

A tentative P-T diagram of liquid - fluid CO_2 constructed on the basis of available data proposes a system of PVT anomalies of CO_2 at 0.5, 1.3 and 2.3 GPa at room Temperature which extends from the melting curve up to at least 1000°C. The three anomaly boundaries show a slight negative dP/dT slope. In principle this system is very like that one found of H_2O, and similarly, the proposed PVT anomalies are interpreted to be structural changes in CO_2.

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