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Anomalous high pressure behaviour of H_2O evidenced by dehydration reactions, H_2O compression and ice melting experiments

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H_2O is the most important component of the fluid phase in mineral reactions and geological processes in the Earth crust and mantle. Its properties may be determined either directly by in-situ methods (e.g. PVT, spectroscopical, electrical measurements) or/and indirectly by the determination of the P-T-course of reaction boundaries in hydrous mineral systems. The P-T course of a reaction boundary is continuous as long all participating components exhibit no discontinuous property behaviour. A deviation of this behaviour is indicated by an irregularity in the P-T course of the boundary.

An experimental study comprising different dehydration reactions was performed up to 3.5 GPa covering the temperature range 0 - 1100˚C. In addition, water compression experiments were conducted between 0 - 80˚C up to 1.5 GPa, and, very recently, the melting curves of ice III and VI have been re-examined in detail.

The in situ experiments were performed with a conventional piston cylinder apparatus, equipped with a logger system able to monitor continuously piston displacement and pressure change (resolution of pressure ±2 MPa, of piston displacement: ±2*10-4mm). Both, temperature and pressure could be run at different rates, in response to the speed of the reaction investigated. For the low temperature experiment a compression cell set up was used, the high temperature experiments were performed with a conventional NaCl-pressure cell, controlled by Ni/CrNi thermocouples.

The temperature frame of this high pressure study between 0-1000˚C was lined out by the following dehydration and dehydration melting reactions:

1) $NaCl*2H_2O = NaCl + 2H_2O$ (temperature range: 0-30˚C)(Mirwald, 2005a);

2) $CaSO_4*2H_2O$ (gypsum) = $CaSO_4*$ 0.5 H_2O (bassanite)+ 1.5 H2O = $CaSO_4$ + $2H_2O$(anhydrite) (50 - 250˚C)(Mirwald, 2008)

3) 2AlO(OH) (diaspor) = Al_2O_3 (corundum) + H_2O (400-600˚C) (Mirwald, 2007)

4) $Mg(OH)_2$ (brucite) = MgO (periclase) + H_2O (700-1100˚C)(Mirwald, 2005b).

The dehydration reactions 2) to 4) revealed a system of inflections to be related to three anomaly boundaries of H_2O at 1.0, 1.8 and 2.7 GPa. Above 120˚ C these anomaly boundaries are almost temperature independent. In the low temperature range the reaction 1) shows similar inflections, however, at different pressure levels, at 0.3, 0.8 and at 1.2 GPa. While the lowest boundary inflection at 0.3 GPa may be correlated with the anomaly boundary at 1 GPa ($>$120˚ C), the two other inflections, at 0.8 an1.2 GPa merge and lead into the boundary at 1 GPa. Thus, in contrast to the high temperature range, both anomalies show a considerable temperature dependence in the low temperature range. The third, uppermost anomaly boundary at 2.7 GPa of the high temperature range seems to intersect the melting curve of ice VII. This anomaly pattern at low temperatures derived from the results of reaction 1) is confirmed: i) by water compression measurements (Mirwald 2005a) in which compressibility anomalies were encountered at 0.3-04 and 0.8 GPa and ii) by recent results of a detailed melting curve study of ice III and VI. While the melting curve of ice III shows an inflection at 0.29 GPa, the ice VI melting curve exhibits two inflections, at 0.7 and at 1,2 GPa.

The compression measurements and the recent observations on the ice melting curves are the clear proof that the anomalies are related to H_2O. Detailed analysis of the inflections of the gypsum – bassanite boundary (Mirwald 2008) and that one of the ice III melting curve suggest that these anomalies are related to a strong entropy increase of H_2O within the pressure range of the inflections. This is likely to be related to a drastic increase of the fluctuations within the hydrogen network of H_2O leading in each case to a state of different H_2O properties.

The observation that these anomalies extend far into the high temperature regime of the fluid state of H_2O is of considerable significance for the mineralogy and petrology as well as for many geological processes in the lower crust and upper mantle of the Earth.

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