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EXPERIMENTAL INVESTIGATION IN THE SYSTEM PORTLANDITE [CA(OH)2] – H_2O AT HIGH TEMPERATURES AND PRESSURES

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Portlandite, $Ca(OH)_2$ a very important mineral compound in the field of building materials belongs to the group of hydroxides of the brucite structure type. In contrast to brucite, $Mg(OH)_2$ of which the P-T stability is limited by the decomposition reaction to periclase (NaCl structure type) + H_2O, portlandite shows hydrous melting. This melting curve is characterised by a very steep negative dP/dT slope (fig.1: B). In presence of excess H_2O melting of portlandite occurs at minimum temperatures being characterised, in addition, by a considerable shallower negative dP/dT slope. Both melting curves, the hydrous melting and the minimum melting in excess of H_2O as well have been outlined up to 30 kb by Irving et al. (1977). Recently, Bai et al. (1994) undertook a detailed study of this system at low pressures. Delineating the melting curves up to 0.65 kb pressure they discovered in addition a solid state transitions referring the high temperature phase as to $Ca(OH)_2$ II. Very recently, the brucite dehydration reaction has been re-examined in very detail up to 30 kb pressure (Mirwald, 2004). This study revealed a non-smooth P-T behaviour of the brucite dehydration boundary by exhibiting three inflections at 11, 19 and 27 kb. These inflections were related to anomalous PVT-behaviour of H_2O. Portlandite which is isostructural with brucite is expected to show a similar response to property changes of H_2O in principle. The P-T range of melting is at lower temperature but in close vicinity to the brucite decomposition boundary. For this study the melting curve of $Ca(OH)_2$ in excess of H_2O was preferred for experimental reasons. Its shallower boundary slope compared to the hydrous melting curve allows a more reliable experimental determination of the fine structure of the melting boundary. Here the preliminary results of this study are reported.

The experiments were conducted in a conventional piston cylinder apparatus up to 30 kb pressure using a conventional NaCl cell assembly. 50 to 100 mg of $Ca(OH)_2$ of reagent grade with some 15 mg of H_2O were welded shut in gold capsules. A Ni-CrNi thermocouple served for temperature reading of an estimated accuracy of ±2K. The reaction was monitored by differential pressure analysis (DPA) technique (Mirwald & Massonne, 1980). While the relative precision of this technique is at 10 bar the stated pressure accuracy of the gauge is ±200 bars. All parameters, pressure change, piston displacement, temperature and time, were simultaneously recorded by a logger system.

The preliminary results of this investigation are given in fig.1 in comparison with literature data. The minimum melting curve of portlandite + H_2O follows very precisely the outlining data by Irving et al. (1977). The detailed P-T mapping of the boundary revealed, however, three inflections at 9, 19 and 27 kb. In addition to the minimum melting curve [$Ca(OH)_2$ + H_2O = melt) it was possible to confirm the $Ca(OH)_2$ I/II transition reported by Bail et al. (1994) and to obtain further data towards higher pressure. This $Ca(OH)_2$ transition boundary shows at 11 kb a reverse in slope and intersects with the minimum melting curve at 22 kb. In addition indications of a further transition of $Ca(OH)_2$ I at high pressure are obtained, of which the boundary course is not well determined so far (cf. fig.1: $Ca(OH)_2$?). It also has a triple point with the melting curve at 32 kb. This phase could not be quenched, so structural aspects remain open. In fig.1 also the recent results obtained on the brucite dehydration are displayed (cf. fig.1: C). It is striking that the inflections observed on the melting boundary of (portlandite + H_2O) are located at the same pressures as determined on the brucite decomposition boundary. This allows to assume that these three inflections on the portlandite melting curve may be related with those on the brucite dehydration boundary. Furthermore, this insinuates that all the inflections are related to anomalous PVT behaviour of H_2O. Inter-

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connection of the inflections observed at the three different pressure levels suggest three boundaries separating four P-T areas of different anomalous PVT behaviour of H_2O (cf. fig.1: I – IIII). The almost temperature independent boundaries extent over a considerable temperature range between 500 and 1100°C, thus lining out a tentative P-T diagram of H_2O.

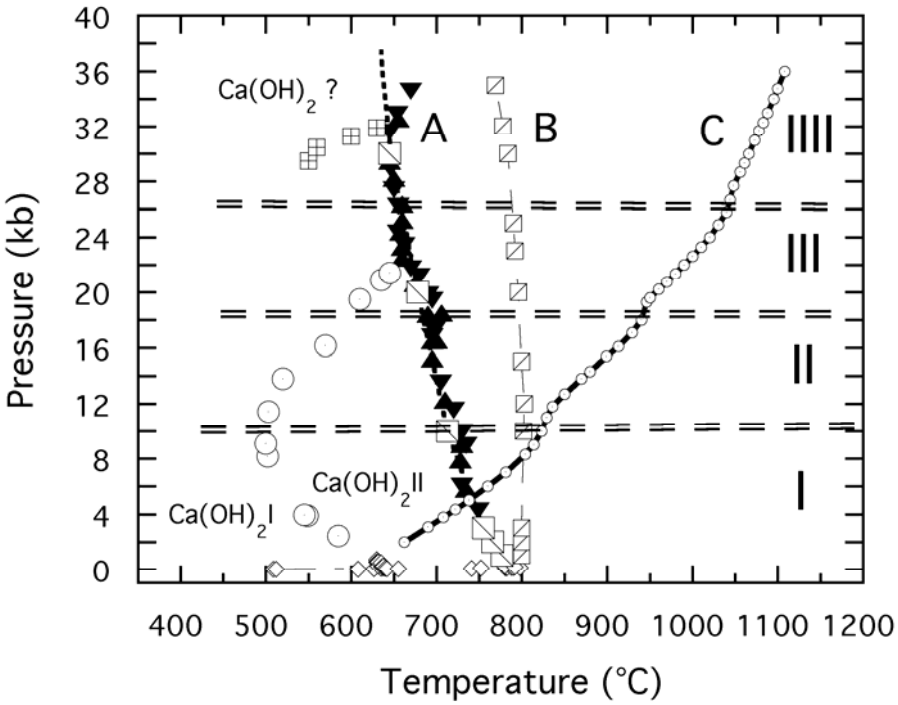

Figure 1: Synoptic diagram of the experimental and literature data. Curve A: melting of periclase + H_2O; solid triangles with tip upward: increasing run temperature; triangle tip downward: decreasing run temperature. Large circles: $Ca(OH)_2$ I – $Ca(OH)_2$ II transition. Squares with cross: transition $Ca(OH)_2$ I – $Ca(OH)_2$?. Large squares with diagonal: melting of periclase + H_2O (Irving et al., 1977); small squares with diagonal (curve B): melting of periclase (Irving et al., 1977); open diamonds: Bai et al. (1994). Curve C (small circles): Mg(OH)2 dehydration boundary (Mirwald, 2004). Dashed double lines: proposed anomaly boundaries of H_2O separating four different areas of PVT-behaviour, I, II, III, IIII. Details see text.

The very flat dP/dT slope of the boundaries indicates that the pressure parameter is dominant which allows to assume that the inflections and the boundaries respectively represent a small densifications of H_2O. The three anomaly boundaries which separate four different PVT states of H_2O are likely to indicate each a structural change of H_2O. A qualitative analysis of the portlandite melting curve in excess of H_2O [$Ca(OH)_2$ + H_2O = melt] and of the brucite dehydration boundary [$Mg(OH)_2$ = MgO + H_2O] on the basis of the Clausius-Clapeyron relation ($dP/dT = \Delta S/\Delta V$) shows that the entropy term plays a dominant role. This indicates that ordering phenomena in H_2O might be essential.

With respect to the geological relevance, this finding will result into small changes of the general topology of phase relations only. However, considerable implications are to be assumed for dynamic hydrous processes which cross these boundaries. Due to property changes of H_2O one may expect non smooth changes of all other, closely related properties, such as the H_2O activity, element partitioning, melting behaviour etc. in the corresponding depths of 30-35, 60-65, and about 90 km of the Earth crust and mantle.

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Artikel/Article: Experimental investigation in the system portlandite [CA(OH)2] - H20 at high temperatures and pressures 268-269