Experimental investigation in the system portlandite [Ca(OH)$_2$] – H$_2$O at high temperatures and pressures

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Portlandite, Ca(OH)$_2$, belongs to the group of hydroxides of the brucite structure type. In contrast to many other hydroxides of which the P-T stability is limited by the decomposition reaction to an oxide + H$_2$O, portlandite shows hydrous melting. In presence of excess H$_2$O the melting of portlandite occurs at minumum temperatures. This "wet" melting boundary is characterised by a considerably shallower negative dP/dT slope compared to the hydrous melting curve. Both melting curves have been outlined up to 30 kb by Irving et al. (1977) and Bai et al. (1994).

The experiments were conducted in a conventional piston cylinder apparatus up to 30 kb pressure using a NaCl cell assembly with a Ni-CrNi thermocouple. 50 to 100 mg of Ca(OH)$_2$ and 15 mg of H$_2$O welded shut in gold capsules served as samples. The dehydration - rehydration reaction was monitored by differential pressure analysis (DPA) - technique (Mirwald & Massonne, 1980).

The results of this investigation compare well with the "wet" melting curve of portlandite outlined by Irving et al. (1977) and Bai et al. (1994). The detailed P-T mapping revealed, however, a fine structure of the melting boundary. Three inflections at 9/715˚, 19/700˚ and 27kb/660˚ C, and two triple points at 22/660˚ and 32 kb /640˚ C have been determined. A solid phase transition reported by Bail et al. (1994) and referred to as Ca(OH)$_2$ I/II transition can be confirmed and has been traced towards higher pressure. In addition two further transition of two non quenchable phases were observed which were preliminarily termed Ca(OH)$_2$ II/* and Ca(OH)$_2$ */**. These two transitions boundaries intersect the melting curve in those triple points at 22 and 32 kb.

Very recently, the brucite dehydration reaction, $Mg(OH)_2 = MgO + H_2O$ has been re-examined in very detail up to 30 kb pressure (Mirwald, 2004). That 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 supercritical H_2O. A comparison of the present $Ca(OH)_2$ melting data and the $Mg(OH)_2$dehydration boundary reveals that the inflections observed are located at the same pressures (9, 19 and 27 kb). Based on this observation the inflections of the "wet" $Ca(OH)_2$ melting curve are correlated with those of the brucite dehydration boundary, assuming that also the inflections of the Ca(Oh)s melting curve are due to anomalous PVT behaviour of supercritical H_2O.

A synopsis of the different data suggests three anomalous boundaries of almost temperature independent course separating four P-T areas of different PVT behaviour of supercritical H_2O, which cover the temperature range between 600 and 1100˚C. The almost temperature independent dP/dT slope of the three H_2O anomaly boundaries indicates that the inflections represent a small densification. Based on the Clausius-Clapeyron relation (dP/dT = $\Delta S/\Delta V$) a qualitative analysis of the decomposition curves of portlandite as well as of the brucite dehydration boundary in the P-T range of the inflections has been conducted. The analysis suggests that the entropy term plays an important role what indicates that the anomaly boundary are likely to be related to structural changes of H_2O.

With respect to the geological relevance of this finding, only small changes in the topology of equilibrium phase relations of hydrous assemblages are given. However, considerable effects are to be assumed for dynamic processes. A crossing of the anomaly boundaries implies changes in H_2O properties and these are relevant for e.g. its activity as well for its solubility and partitioning properties.

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