



Dehydration study of gypsum-bassanite-anhydrite up to 3.5 GPa - indication of PVT anomalies of water at high pressure

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Water, plays an eminent role in geochemistry. Besides its existence as a free compound it is an essential component in many minerals. Hydration and dehydration reactions play an important role in geological processes. The P-T boundary of such reactions allows to obtain information on the physical-chemical properties of the participating phases. Continuing a previous study on the dehydration of gypsum to bassanite ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} + 1.5\text{H}_2\text{O}$) (Mirwald, 2003), the work was extended on the hydration/dehydration equilibrium of bassanite - anhydrite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} = \text{CaSO}_4 + 0.5\text{H}_2\text{O}$). The study covers the P-T range up to 3.5 GPa and 80 – 280° C.

The experiments were conducted in a conventional piston cylinder apparatus using a NaCl cell assembly with a Ni-CrNi thermocouple. 130 mg of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and 13 mg of H_2O welded shut in gold capsules served as sample. The dehydration – rehydration reaction was monitored by differential pressure analysis (DPA) - technique (Mirwald, 2005 a, b).

The data obtained are in good agreement with a previous study (Yamamoto & Kennedy, 1967). However, a closer inspection reveals that each of the two dehydration/hydration boundaries exhibit three distinct inflections at 0.9, 1.6-1.7 and 2.7 GPa. While gypsum shows in the pressure range investigated no phase transition (Stretton et al. 1997), a high pressure transition is reported for anhydrite at 2.0 GPa (Borg & Smith, 1997). Compression data on bassanite are not available. As already previously supposed, the most conclusive explanation for the inflections of the dehydration

boundaries are PVT anomalies of H₂O (Mirwald, 2003). The six inflections suggest three anomaly boundaries of little temperature dependence in the studied temperature range of 100 – 300° C.

The findings of this work are in good agreement with a very recent compressibility study on water in the range up to 80° C (Mirwald, 2005 a), an investigation on the breakdown of albite in presence of small amounts of H₂O (NaAlSi₃O₈; temperature range 450 - 1100° C) (Mirwald 2005 c), and dehydration studies of portlandite (Ca(OH)₂; temperature range: 600-800° C) (Mirwald, 2005 d) and of brucite (Mg(OH)₂; temperature range 700 – 1200° C)(Mirwald, 2005 b) where similar effect were observed. A synopsis of these different studies allows to line out a tentative phase diagram of H₂O that is characterised by four pressure ranges of different PVT-properties within the P-T range up to 3.5 GPa and 1200° C.

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 rock forming processes, since crossing of an anomaly boundary implies changes of the physical-chemical properties of H₂O, such as e.g. activity, solubility and partitioning properties .

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