The fine-structure of the dehydration boundary of brucite (Mg(OH)$_2$) up to 3.5 GPa – indication of anomalous PVT behaviour of supercritical H$_2$O

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Abstract: Liquid and supercritical H$_2$O, the most abundant and important non-crystalline component in rock forming processes, is assumed to exhibit continuous PVT behaviour at high pressures and temperatures. However, a number of experimental observations at high pressure and temperatures challenges this concept. Direct measurements of PVT properties of H$_2$O at supercritical conditions are very difficult. Information on the PVT behaviour at these P-T conditions may be gained by certain dehydration reactions. An experimental re-examination of the reaction Mg(OH)$_2$ (brucite) = MgO (periclase) + H$_2$O has been conducted between 0.4 to 3.5 GPa and 650 to 1200°C. The study was performed with a piston cylinder apparatus using the in-situ differential pressure analysis (DPA)-technique. The data reveal that the P-T slope of the equilibrium boundary is not continuous but exhibit a fine-structure which is characterised by three inflections at 1.1 GPa/830°C, 1.9 GPa/945°C and 2.7 GPa/1040°C. Because the solid phases, Mg(OH)$_2$ and MgO, exhibit no structural changes at these conditions, these effects are thought to be due to anomalous PVT behaviour of supercritical H$_2$O.

Key-words: brucite dehydration, not-smooth P-T boundary, anomalous PVT properties of H$_2$O.

Introduction

The abundant occurrence of hydrous minerals, fluid inclusions in minerals and fluid films on intergranular grain boundaries of rocks demonstrates the importance of H$_2$O as a chemical component of the Earth's crust and mantle. Its relevance as a component in dehydration-hydration and melting processes and as vapour phase in solid state reactions has been shown in numerous studies and comprehensively discussed under mineralogical and petrological aspects (*e.g.* Ringwood, 1975; Thompson, 1992, Vielzeuf & Schmidt, 2001). The concept of liquid and supercritical H$_2$O at high P and T, is based on the assumption of continuous PVT behaviour (*e.g.*, Bridgman, 1912; Burnham *et al.*, 1969; Kerrick & Jacobs, 1981; Halbach & Chattterjee, 1982; Haar *et al.*, 1984; Saul & Wagner, 1989). However, a number of high pressure studies in the subcritical P-T range of H$_2$O provide observations of anomalous behaviour which may be attributed to structural changes in water (*e.g.*, Adams, 1931; Yamamoto & Kennedy, 1969; Okulkov *et al.*, 1994; Bellissent-Funel, 1998; Soper & Ricci, 2000; Krisch *et al.*, 2002; Mirwald, 2001, 2002, 2003; Kawamoto *et al.*, 2004).

Also in the P-T range of supercritical behaviour of H$_2$O a multitude of mineralogical and petrological observations has been documented in experimental studies of mineral reactions in presence of H$_2$O in which slight irregularities in the boundary course or pronounced slope changes insinuate anomalous behaviour of H$_2$O (*e.g.*, Merrill *et al.*, 1970; Mirwald & Massonne, 1980; Goldsmith & Jenkins, 1985; Kawamoto *et al.*, 2003; Hill & Boettcher, 1970; Modreski & Boettcher, 1972; Mysen & Boettcher, 1976; Wyllie & Wolf, 1993; Vielzeuf & Schmidt, 2001). All these observations challenge the concept of continuous PVT behaviour of H$_2$O.

The direct and quantitative determination of PVT properties of H$_2$O at high P-T conditions poses considerable experimental problems (*e.g.*, Maier & Frank, 1966; Köster & Frank, 1969; Burnham *et al.*, 1969; Hilbert, 1979; Brodholt & Wood, 1994). Dehyration/hydration equilibria offer a qualitative method to trace the PVT properties of H$_2$O, because the equibrium boundary reflects the thermodynamic parameters of all participating phases. The reaction brucite (Mg(OH)$_2$ = periclase (MgO) + H$_2$O has been chosen for this purpose. Its P-T-shape has originally been established by Irving *et al.* (1977), Schramke *et al.* (1982), Aranovich & Newton (1996). The two solid phases involved are characterised by a densely packed structure and show no phase transitions up to 3.5 GPa (Xia *et al.*, 1998; Zhan, 2000). Based on these data a continuous change in volume and caloric properties has to be expected along the boundary. Thus, irregularities in the dP/dT course of this equilibrium boundary are to be related with the H$_2$O component.

Experimental

The experiments were conducted with an endloaded piston-cylinder apparatus using a 12 mm bore vessel and a conventional NaCl cell assembly (Mirwald *et al.*, 1975). The tem-