In situ X-ray diffraction investigation of lawsonite and zoisite at high pressures and temperatures

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ABSTRACT

The $P$-$V$-$T$ behavior of synthetic lawsonite [CaAl$_2$(Si$_2$O$_7$)(OH)$_2$·H$_2$O] and synthetic zoisite [Ca$_3$Al$_2$(SiO$_4$)(Si$_2$O$_7$)O(OH)] has been determined under high pressures and high temperatures up to 7 GPa and 1000 °C using a MAX 80 cubic anvil high-pressure apparatus. Several experimental runs were carried out for both minerals, first compressing the samples at room temperature and then heating them until a breakdown reaction occurred. Generally, the samples were mixed with vaseline to ensure hydrostatic pressure transmitting conditions, NaCl served as an internal standard for pressure calibration. The pressure data at room temperature were fitted to a Birch-Murnaghan equation of state ($K_0'$ assumed to be 4), yielding isothermal bulk moduli $K_{0}'$ = 106.7 ± 1.3 GPa for lawsonite and 125.1 ± 2.1 GPa for zoisite, respectively. These values agree well with recent results. The high-temperature high-pressure data were fitted to the high-temperature Birch-Murnaghan equation of state. In contrast to other investigations, $(\partial K_T/\partial T)_P$ is slightly negative for lawsonite. The sign is not affected by considering the thermal expansion data at ambient pressure. Similar calculations for zoisite yielded a positive $(\partial K_T/\partial T)_P$ without using high-temperature data at atmospheric pressure whereas a negative sign resulted from calculations taking into account the 1 bar thermal expansivity. Calculations of several mineral equilibria involving zoisite and lawsonite with the Berman data set supplemented by the $P$-$V$-$T$ data presented here correspond well to experimentally determined pressure stability limits of these phases.

INTRODUCTION

During the last decade the availability of internally consistent databases (e.g., Berman 1988; Holland and Powell 1990) has become an important tool for the understanding of processes in the Earth’s crust and mantle. Although the techniques used to derive these data sets are very different, thermodynamic calculations at pressures up to 1 GPa yield almost similar results in most cases. On the other hand, extrapolation of equilibrium curves to $P$-$T$ conditions of the lower crust and upper mantle are sometimes quite inconsistent with respect to $dP/dT$ slope and absolute position especially for reactions containing hydrous phases. The most probable reasons for this behavior are (1) the currently used equations of state (EOS) for H$_2$O are mainly based on extrapolations of low-pressure data and tend to predict different H$_2$O volumes at higher pressures (cf. Holland et al. 1996), and (2) due to the lack of thermophysical data (that means basically data on bulk modulus, $K_T = -V(\partial P/\partial V_T)$, and thermal expansivity $\alpha$) of several high-pressure hydrous phases 10 years ago, parameters describing the $P$-$V$-$T$ behavior of these phases had to be estimated.

Since then, significant advances in high-pressure techniques made it possible to improve the situation, and $K_T$ as well as the volumetric behavior at elevated pressure and temperature of many high-pressure hydrous phases have been measured recently (e.g., Comodi et al. 1992; Pawley et al. 1995; Comodi and Zanazzi 1996; Holland et al. 1996; Grevel et al. 1997; Comodi and Zanazzi 1997; Bose and Navrotsky 1998; Daniel et al. 1997, 1998; Grevel et al. 1998; Pawley et al. 1998). The volumetric behavior of the Ca-minerals zoisite [Ca$_3$Al$_2$(SiO$_4$)(Si$_2$O$_7$)O(OH)] and lawsonite [CaAl$_2$(Si$_2$O$_7$)(OH)$_2$·H$_2$O] is of particular interest because these are stable to pressures of ~7 GPa and more (Pawley et al. 1999; Schmidt and Poli 1994; Skrok et al. 1994; Poli and Schmidt 1998), and calculations using the internally consistent databases cited above could not explain the $P$-$T$ conditions (Grevel 1998). Results for bulk modulus differ significantly. Holland et al. (1996) found $K_T$ of 279 ± 9 GPa for zoisite and 191 ± 5 GPa for lawsonite, respectively, from powdered samples in a diamond anvil cell at a synchrotron source, whereas Comodi and Zanazzi (1996, 1997) reported much smaller values from single-crystal X-ray diffraction experiments: $K_T$ (zoisite) = 102 ± 6.5 GPa and $K_T$ (lawsonite) = 98.2 ± 2 GPa. This has been addressed by combining high-pressure and high-temperature techniques by Pawley et al. (1998, in preparation); Additionally, Daniel et al. (1998) published some preliminary results of their in-situ high $P$-$T$ angle-dispersive X-ray diffraction measurements of lawsonite. In view of these experiments the results of Holland et al. (1996) seem to be wrong, but still some discrepancies remain concerning the bulk moduli. The present work presents additional in-situ data on zoisite and lawsonite and discusses inconsistencies in the data sets.