

## Calibration of zircon as a Raman spectroscopic pressure sensor to high temperatures and application to water-silicate melt systems

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### ABSTRACT

The shifts in wavenumber of the  $\nu_3(\text{SiO}_4)$  ( $\sim 1008 \text{ cm}^{-1}$ ) Raman band of fully crystalline synthetic zircon with changing pressure ( $P$ ) and temperature ( $T$ ) were calibrated for application as a Raman spectroscopic pressure sensor in optical cells to about 1000 °C and 10 GPa. The relationship between wavenumber ( $\nu$ ) of this band and  $T$  from 22 to 950 °C is described by the equation  $\nu \text{ (cm}^{-1}\text{)} = 7.54 \cdot 10^{-9} \cdot T^3 - 1.61 \cdot 10^{-5} \cdot T^2 - 2.89 \cdot 10^{-2} \cdot T + 1008.9$ , where  $T$  is given in °C.

The pressure dependence is nearly linear over the studied range in  $P$ . At  $\sim 25$  °C, the  $\partial\nu/\partial P$  slope to 6.6 GPa is  $5.69 \text{ cm}^{-1}/\text{GPa}$ , and that to 2 GPa is  $5.77 \text{ cm}^{-1}/\text{GPa}$ . The  $\partial\nu/\partial P$  slope does not significantly change with temperature, as determined from experiments conducted along isotherms up to 700 °C. Therefore, this pressure sensor has the advantage that a constant  $\partial\nu/\partial P$  slope of  $5.8 \pm 0.1 \text{ cm}^{-1}/\text{GPa}$  can be applied in experiments to pressures of at least about 6.6 GPa without introducing a significant error. The pressure sensor was tested to determine isochores in experiments with  $\text{H}_2\text{O} + \text{Na}_2\text{Si}_3\text{O}_7$  and  $\text{H}_2\text{O} + \text{NaAlSi}_3\text{O}_8$  fluids to 803 °C and 1.65 GPa. These pressures were compared to pressures calculated from the equation of state (EoS) of  $\text{H}_2\text{O}$  based on the measured vapor dissolution or ice melting temperature for the same experiment. Pressures determined from the zircon sensor in runs in which  $\text{NaAlSi}_3\text{O}_8$  melt dissolved in aqueous fluid were close to or lower than the pressure calculated from the EoS of  $\text{H}_2\text{O}$  using the vapor dissolution or ice melting temperature. In experiments with  $\text{H}_2\text{O} + \text{Na}_2\text{O} + \text{SiO}_2$  fluids, however, the pressure obtained from the Raman spectrum of zircon was often significantly higher than that estimated from the EoS of  $\text{H}_2\text{O}$ . This suggests that the pressures along some critical curves of water–silicate melt pseudobinary systems should be revised.

**Keywords:** Zircon, Raman spectroscopy, temperature, pressure sensor, diamond-anvil cell