Optimizing Raman spectral collection for quartz and zircon crystals for elastic thermobarometry

Mayara F. Cizina[1], T. Dylan Mikesell[1], and Matthew J. Kohn[1,*]

[1]Department of Geosciences, Boise State University, Boise, Idaho 83725, U.S.A.

Abstract

Raman spectroscopy is widely used to identify mineral and fluid inclusions in host crystals, as well as to calculate pressure-temperature (*P-T*) conditions with mineral inclusion elastic thermobarometry, for example quartz-in-garnet barometry (QuiG) and zircon-in-garnet thermometry (ZiG). For thermobarometric applications, *P-T* precision and accuracy depend crucially on the reproducibility of Raman peak position measurements. In this study, we monitored long-term instrument stability and varied analytical parameters to quantify peak position reproducibility for Raman spectra from quartz and zircon inclusions and reference crystals. Our ultimate goal was to determine the reproducibility of calculated inclusion pressures ("P_{inc}") and entrapment pressures ("P_{trap}") or temperatures ("T_{trap}") by quantifying diverse analytical errors, as well as to identify optimal measurement conditions and provide a baseline for interlaboratory comparisons. Most tests emphasized 442 nm (blue) and 532 nm (green) laser sources, although repeated analysis of a quartz inclusion in garnet additionally used a 632.8 nm (red) laser. Power density was varied from <1 to >100 mW and acquisition time from 3 to 270s. A correction is proposed to suppress interference on the ~206 cm^{-1} peak in quartz spectra by a broad nearby (~220 cm^{-1}) peak in garnet spectra.

Rapid peak drift up to 1 cm^{-1}/h occurred after powering the laser source, followed by minimal drift (<0.2 cm^{-1}/h) for several hours thereafter. However, abrupt shifts in peak positions as large as 2–3 cm^{-1} sometimes occurred within periods of minutes, commonly either positively or negatively correlated to changes in room temperature. An external Hg-emission line (fluorescent light) can be observed in spectra collected with the green laser and shows highly correlated but attenuated directional shifts compared to quartz and zircon peaks. Varying power density and acquisition time did not affect Raman peak positions of either quartz or zircon grains, possibly because power densities at the levels of inclusions were low. However, some zircon inclusions were damaged at higher power levels of the blue laser source, likely because of laser-induced heating.

Using a combination of 1, 2, or 3 peak positions for the ~128, ~206, and ~464 cm^{-1} peaks in quartz to calculate P_{inc} and P_{trap} showed that use of the blue laser source results in the most reproducible P_{trap} values for all methods (0.59 to 0.68 GPa at an assumed temperature of 450 °C), with precisions for a single method as small as ±0.03 GPa (2σ). Using the green and red lasers, some methods of calculating P_{trap} produce nearly identical estimates as the blue laser with similarly good precision (±0.02 GPa for green laser, ±0.03 GPa for red laser). However, using 1- and 2-peak methods to calculate P_{trap} can yield values that range from 0.52 ± 0.06 to 0.93 ± 0.16 GPa for the green laser, and 0.53 ± 0.08 GPa to 1.00 ± 0.45 GPa for the red laser. Semiquantitative calculations for zircon, assuming a typical error of ±0.25 cm^{-1} in the position of the ~1008 cm^{-1} peak, imply reproducibility in temperature (at an assumed pressure) of approximately ±65 °C.

For optimal applications to elastic thermobarometry, analysts should: (1) delay data collection approximately one hour after laser startup, or leave lasers on; (2) collect a Hg-emission line simultaneously with Raman spectra when using a green laser to correct for externally induced shifts in peak positions; (3) correct for garnet interference on the quartz 206 cm^{-1} peak; and either (4a) use a short wavelength (blue) laser for quartz and zircon crystals for *P-T* calculations, but use very low-laser power (<12 mW) to avoid overheating and damage or (4b) use either the intermediate wavelength (green; quartz and zircon) or long wavelength (red; zircon) laser for *P-T* calculations, but restrict calculations to specific methods. Implementation of our recommendations should optimize reproducibility for elastic geothermobarometry, especially QuiG barometry and ZiG thermometry.

Keywords: Raman spectroscopy, elastic thermobarometry, garnet, quartz, zircon