Evaluation of residual pressure in an inclusion–host system using negative frequency shift of quartz Raman spectra

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ABSTRACT

Raman spectra of quartz inclusions in garnet hosts of low-pressure/temperature metamorphic rocks from the Yanai district in the Ryoke belt (around 0.1–0.3 GPa/500–600 °C), Southwest Japan, exhibit frequency (peak position) shifts toward lower wavenumbers as compared to those of a quartz standard measured at ambient conditions. The observed negative frequency shifts indicate that tensile normal stress is exerted on the quartz–garnet boundary and therefore, quartz inclusions are subjected to negative residual pressure. Elastic modeling that assumed the constant elastic properties of minerals cannot explain this negative residual pressure. This study estimated the residual pressure based on a new scheme of elastic modeling with equation of state (EOS) of quartz and garnet, which takes into account the pressure- and temperature-dependency of compressibility and expansivity. The calculated residual pressure was converted into frequency shifts of quartz Raman spectrum based on the experimentally determined relation. The results showed that the quartz inclusions in garnets retain residual pressure of about –0.3 GPa, and logically reproduced the observed frequency shifts in the direction of lower wavenumbers. The new elastic modeling also simulates positive frequency shifts retained by quartz inclusions in garnets of high-pressure metamorphic rocks from the Sambagawa metamorphic belt in Southwest Japan, and from the Motagua fault zone in Guatemala. The degree and direction of Raman frequency shifts of quartz inclusion in garnet depend on metamorphic conditions when the quartz was included in the host garnet. Conversely, the metamorphic conditions prevailing when a set of a quartz inclusion and garnet host was recrystallized can be inferred from Raman frequency shifts of quartz inclusion in garnet. The proposed Raman spectroscopic analysis should be a powerful and useful tool to decipher information at earlier stage of garnet growth even in samples of highly recrystallized matrix phases during exhumation and retrograde stages.

Keywords: Raman spectroscopy, negative residual pressure, Ryoke metamorphic rocks, quartz, garnet, equation of state

INTRODUCTION

Mineral or fluid inclusions within host minerals preserve information related to the metamorphic history during the growth of the host mineral. In general, these metamorphic conditions are constrained using mineral reactions or thermodynamic calculations based on the analysis of the chemical compositions of the host and inclusion (e.g., Whitney et al. 1995; Katayama et al. 2000; Tsunogae and Santosh 2006). On the other hand, the physical properties of the host and inclusion can also be used to estimate the metamorphic conditions. One of those techniques involves the analysis of residual pressure. Each mineral has distinct compressibility and expansivity characteristics. Consequently, after inclusion is incorporated to the host mineral, both phases will follow different volume change paths according to change in surrounding pressure-temperature (P–T) conditions. This volume difference in the inclusion–host system, designated as residual pressure (or internal stress), can be detected as a change in the Raman frequencies (i.e., peak positions) and/or widths (e.g., Hemley 1987; Parkinson and Katayama 1999; Nasdala et al. 2005; Kagi et al. 2009). Raman spectroscopy can analyze confined materials without sample destruction if the sample is transparent to visible light. Therefore, this technique is appropriate for detecting the residual pressure preserved in the inclusion within the host mineral. Izraeli et al. (1999) detected the residual pressure by measuring the Raman frequency shifts of olivine inclusions in diamond from the Udachnaya mine in Siberia, and estimated the metamorphic pressure using bulk modulus, shear modulus, and thermal expansion parameters of inclusion and host minerals. Sobolev et al. (2000) also detected the residual pressure by measuring the Raman frequency shifts of small coesite inclusions in diamond from Venezuela, and estimated...