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Construction of Raman geothermobarometer using aluminosilicate minerals in garnet porphyroblast

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In recent years, the development of geothermobarometer applying Raman spectroscopy has been actively examined. Several studies report the detection of new information of the metamorphic history that was difficult to obtain using conventional thermodynamic approaches. Especially, the "quartz Raman barometer" that can constrain the metamorphic condition using Raman peak shifts of quartz inclusions in garnet porphyroblasts show remarkable achievements in the Sambagawa belt. However, quartz transforms to coesite or β -quartz under the ultrahigh-pressure or high-temperature conditions, respectively, and applicable geological zone is limited. In the present study, we focused on aluminosilicate minerals, sillimanite and kyanite, in garnet porphyroblasts and examined whether the metamorphic condition can constrain using these Raman spectra as with quartz Raman barometer.

First, we calculated the relation between the metamorphic *P-T* condition and residual pressure using the elastic moduli of sillimanite, kyanite, and garnet. As a result, the residual pressure of sillimanite in garnet is independent of pressure condition, and depends on only temperature condition. On the other hand, the residual pressure of kyanite in garnet depends on pressure condition rather than temperature condition. Next, we measured the natural samples of sillimanite and kyanite inclusions in garnet porphyroblasts. Ultrahigh-temperature and high-pressure metamorphic rocks were measured; Garnet-Sillimanite gneiss collected from Rundvagshetta, Lutzow-Holm Complex in eastern Antarctica, and Kyanite-Quartz eclogite collected from Besshi region, Sambagawa belt in central Shikoku. The Raman spectra of sillimanite inclusions in garnets of Garnet-Sillimanite gneiss show characteristic peaks at around 962 and 1182 cm⁻¹, and these peaks shift to high wavenumber side of around 4 to 5 cm⁻¹. The Raman spectra of kyanite inclusions in garnets of Kyanite-Quartz eclogite show characteristic peaks at around 325 and 486 cm⁻¹, and these peaks shift to high wavenumber side of around 1 cm⁻¹.

The residual pressures were estimated to be 0.8 GPa for sillimanite and 0.3 GPa for kyanite using previously reported experimental data of aluminosilicate minerals. The residual pressure value of sillimanite inclusions in ultrahigh-temperature metamorphic rocks is converted to the metamorphic temperature of around $1000\,^{\circ}$ C, and this result is consistent with previous studies. On the other hand, the residual pressure of kyanite inclusions is calculated as negative value with increasing metamorphic pressure, but measured values in high-pressure metamorphic rocks of the Sambagawa belt are positive. The elastic modulus of kyanite selected in the present study seems to have some problems, but it's expected to be solved by improving the equation of state of kyanite. These results indicate that Raman spectra of aluminosilicate minerals are useful to estimate metamorphic condition for high- to ultrahigh-pressure and -temperature metamorphic rocks.

Keywords: Raman geothermobarometer, sillimanite, kyanite, garnet, high-temperature metamorphic rock, ultrahigh-pressure metamorphic rock