A thermobarometer for sphene

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Sphene and zircon are common accessory minerals that exist over a broad P-T range and occur in a variety of crustal rocks, and thus have great potential for use in geothermometry. Both minerals are also used in radiometric age dating, allowing the correlation of age and thermal information. Their essential structural constituents, Ti and Zr, can replace each other to a limited extent and the incorporation of Zr in sphene is expected to depend on temperature (and possibly also pressure) of the system. Calibration of a Zr-in-sphene thermometer was accomplished through a combination of high-pressure-temperature laboratory experiments and analyses of natural sphene grains whose crystallization conditions were independently determined.

Synthetic sphene crystals were grown in the presence of zircon from hydrothermal solutions at 1.0 and 1.8 GPa and 800°-1000°C, and were analyzed for Zr by electron microprobe (EMP). Natural sphene crystals from six different rhyolites (~0.2 GPa) and one amphibolite (~0.5 GPa) were also analyzed for Zr by EMP. The combined results define a log-linear relationship between equilibrium Zr content (ppm by weight), reciprocal absolute temperature, and pressure (GPa):

$$\log(Zr_{sph}) = 10.59 - 7857/T - 920P/T$$

The thermometer shows significant sensitivity to pressure, with Zr in sphene decreasing by a factor of ~5 with a pressure increase of 1 GPa.

Because natural sphene often contains significant amounts of rare-earth elements (REEs) or fluorine and aluminum, several experiments were run to determine if the presence of these elements has an appreciable effect on Zr concentration. Neither REE nor F-Al substitutions resulted in Zr concentrations that deviated from their ‘pure’ counterparts by more than ~12%. This is not expected to result in an over- or underestimation of the crystallization temperature by more than ~15°C.

In summary, the application of this new thermometer to sphene of unconstrained growth conditions has the potential to return crystallization temperatures with an approximate uncertainty of ±25°C over the temperature range of interest in rocks ranging from rhyolitic tuffs to subduction zone migmatites.