

The use of Raman spectroscopy in addressing metastability problems in fluid inclusion microthermometry

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The use of microthermometric measurements of phase-change temperatures to estimate the composition of fluid inclusions is based on the assumption that the phase change occurs at thermodynamic equilibrium. However, in the heating-freezing processes, metastability or thermodynamic disequilibrium is commonly encountered, making certain microthermometric measurements impossible or unreliable for fluid composition calculation. This paper presents case studies in which Raman spectroscopy is used to effectively address some of these problems. Reliable estimation of fluid composition, especially the salinity, is essential for providing a reliable internal standard required for the quantification of trace element analysis by other methods, such as laser ablation inductively coupled plasmas mass spectrometry (LA-ICP-MS).

Incomplete freezing of fluid inclusions is a common metastability phenomenon in microthermometry, which can be detected by the presence of the water band in the Raman spectrum. The recognition of incomplete freezing in the cooling run is crucial in understanding the nature of the “first-melting” temperature in the heating process, which should not be treated as identical to the eutectic temperature. Furthermore, the neglect of incomplete freezing can result in subsequent metastable melting of solid phases, leading to incorrect estimation of the fluid composition and total salinity. Raman spectroscopy can also help determine the last melting phase, especially the distinction between ice, hydrohalite and halite, which is critical in the calculation of salinity.

In cases where metastability is inevitable in microthermometry, estimation of salinity or chlorinity directly from Raman spectroscopy is an alternative and/or preferred method, provided that the equations from the literature are calibrated with synthetic fluid inclusions of known salinity. For example, if a fluid inclusion cannot be frozen, no microthermometric data can be obtained and Raman spectroscopy is the only viable method of estimating the salinity. In cases where microthermometric measurements are stable (i.e., in thermodynamic equilibrium), the salinity calculated from these measurements is considered to be more reliable than that estimated from Raman spectroscopy. Conversely, if the microthermometric data are suspected to be metastable or uncertain (e.g., due to indetermined last-melting phase), the salinity from Raman spectroscopy is considered more reliable than that from microthermometry.