LETTER

Modification of gas speciation in quartz-hosted fluid inclusions by stray laser radiation during LA-ICPMS analysis

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ABSTRACT

Laser-ablation inductively coupled-plasma mass spectrometry (LA-ICPMS) is an established method of analyzing the elemental composition of individual fluid inclusions in minerals. While the method affords good spatial control of ablation pits, we have found that stray light from the UV (193 nm) laser may permanently modify the gas species in adjacent fluid inclusions. We have used Raman spectroscopy to analyze natural fluid inclusions in quartz before and after ablating test pits. New molecular species (CO, H_2 , and O_2) appeared in the vapor phases of inclusions near the pits, resulting in complex, disequilibrium gas mixtures (e.g., CO₂-CH₄-H₂O-CO-H₂-O₂) and formation of iron oxyhydroxides in brine inclusions. Ablation for 40 s with a laser fluence of \sim 24 J/cm² on the sample produced the new gas species in inclusions at various distances up to 210 µm from the pits, depending on pit diameter. We attribute the changes in gas speciation to molecular photodissociation induced by stray UV-laser light. We have no evidence that this artifact changes the bulk elemental composition or density of the affected inclusions. The problem for fluid inclusion analysis is that phase-transition temperatures (e.g., clathrate hydrate dissociation, partial homogenization of the carbonic phases, and total homogenization) are highly sensitive to the mixture of gas species present. This means that parameters such as gas compositions, bulk salinity, and minimum entrapment temperatures are likely to be misinterpreted if inclusions are analyzed by microthermometry or Raman spectroscopy in samples that have already undergone laser ablation.

Keywords: Fluid inclusion, Raman spectroscopy, laser ablation ICP-MS, microthermometry, gas, speciation