American Mineralogist, Volume 103, pages 418–429, 2018

A new optical cell for in situ Raman spectroscopy, and its application to study sulfur-bearing fluids at elevated pressures and temperatures

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Abstract

Sulfur is an important component in volcanic gases at the Earth surface but also present in the deep Earth in hydrothermal or magmatic fluids. Little is known about the evolution of such fluids during ascent in the crust. A new optical cell was developed for in situ Raman spectroscopic investigations on fluids allowing abrupt or continuous changes of pressure up to 200 MPa at temperatures up to 750 °C. The concept is based on a flexible gold bellow, which separates the sample fluid from the pressure medium water. To avoid reactions between aggressive fluids and the pressure cell, steel components in contact with the fluid are shielded by gold foil.

The cell was tested to study redox reactions in fluids using aqueous ammonium sulfate solutions as a model system. During heating at constant pressure of 130 MPa, sulfate ions transform first to HSO_4^- ions and then to molecular units such as H_2SO_4. Variation of pressure shows that the stability of sulfate species relies on fluid density, i.e., highly charged species are stable only in high-density fluids. Partial decomposition of ammonium was evident above 550 °C by the occurrence of a nitrogen peak in the Raman spectra. Reduced sulfur species were observed above 700 °C by Raman signals near 2590 cm^{-1} assigned to HS^- and H_2S. No clear evidence for the formation of sulfur dioxide was found in contrary to previous studies on aqueous H_2SO_4, suggesting very reducing conditions in our experiments. Fluid-mineral interaction was studied by inserting into the cell a small, semi-open capsule filled with a mixture of pyrite and pyrrhotite. Oxidation of the sample assembly was evident by transformation of pyrite to pyrrhotite. As a consequence, sulfide species were observed in the fluid already at temperatures of ~600 °C.

Keywords: In situ Raman spectroscopy, fluids, decompression, optical cell, sulfur speciation, redox reactions