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In-situ characterization of oxalic acid breakdown at elevated *P* and *T*: Implications for organic C-O-H fluid sources in petrologic experiments

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ABSTRACT

Decomposition of oxalic acid in the presence of water was examined in a hydrothermal diamond-anvil cell up to 800 °C and 970–1480 MPa as a function of oxygen fugacity to assess its usefulness as a C-O-H fluid source in petrologic experiments. Fluid, vapor, and solid species were identified in situ at elevated temperature and pressure with Raman spectroscopy and optical microscopy. Under oxidizing conditions (buffered by the reaction $NiO \leftrightarrow Ni+\frac{1}{2}O_2$), oxalic acid decomposes to carbon dioxide and water. Under reducing conditions (buffered by the reaction $Mo+O_2 \leftrightarrow MoO_2$), oxalic acid decomposes to methane and hydrogen. Under unbuffered conditions, at intermediate oxygen fugacity (~0 to 1 log units below the fayalite-quartz-magnetite buffer), oxalic acid disproportionates to graphite and minor methane and carbon dioxide. The results from the Ni-NiO-buffered and Mo-MoO_2-buffered experiments result in observed fluid species that are similar to those predicted by previous investigations. However, there are substantial differences between our results and previous studies of oxalic acid decomposition in the unbuffered experiment that was within a log unit of the fayalite-magnetite-quartz (FMQ) buffer. These include the detection of aqueous C-H species at temperatures as low as 400 °C and a solid graphite-like phase at 800 °C. These differences can be explained if we consider that aqueous H_2 in our experiment reacted to form the C-H species, instead of being lost via diffusion through the H_2-permeable capsules used in previous studies. Consequently, for experiments within about 1 log unit of the FMQ buffer curve, oxalic acid is likely a poor choice for a C-O-H fluid source because the formation of graphitic carbon would result in significant deviations from the expected C-O-H fluid composition and concentration (i.e., CO_2+H_2O). At oxygen fugacities outside a log unit of FMQ, the observed fluid species are similar to those predicted by previous investigations and the use of oxalic acid as a C-O-H fluid source is permissible from the perspective of oxygen fugacity, although other system parameters (e.g., sample geometries, capsule thickness, capsule materials, gasket materials, wall thickness) must still be considered.

Keywords: Hydrothermal diamond-anvil cell, Raman spectroscopy, oxygen fugacity, magmatic volatiles, water, carbon