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The sulfur speciation in S-bearing minerals: New constraints by a combination of electron microprobe analysis and DFT calculations with special reference to sodalite-group minerals

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Abstract

In this work, we present an improved method for the semi-quantitative determination of sulfur species in S-bearing minerals by electron microprobe analysis. For calibration, we analyzed several sulfate and sulfide standard minerals such as baryte, celestine, chalcopyrite, and pyrite, and correlated the results with theoretical calculations retrieved from density functional theory (DFT). We applied this method to natural sodalite-group minerals from various localities. In addition, we applied the more common Raman spectroscopy to some samples and show that this method cannot be applied to sodalite-group minerals to determine their sulfur speciation. We show that even though sodalite-group minerals have a complex crystal structure and are sensitive to the electron beam, electron microprobe analysis is a reliable tool for the analysis of their sulfur speciation. The natural sodalite-group minerals show systematic variations in sulfur speciation. These variations can be correlated with the independently determined oxidation state of the parental magmas thus making S-bearing sodalite-group minerals good redox proxies, although we show that the electron microprobe analysis of the sulfur speciation is matrix-dependent, and the sulfur speciation itself depends on crystal chemistry and structure, and not only on f_{O_2}.

Keywords: Sulfur speciation, igneous, sodalite, oxygen fugacity, electron microprobe, Raman spectroscopy, density functional theory