American Mineralogist, Volume 104, pages 158–161, 2019

## LETTER

## Zinc transport in hydrothermal fluids: On the roles of pressure and sulfur vs. chlorine complexing

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## ABSTRACT

We provide an experimental confirmation of the suggestion, based on thermodynamic simulations and extrapolations (Zhong et al. 2015), that Zn is transported in the form of chloride complexes in most acidic, shallow hydrothermal systems; while bisulfide complexes become increasingly important in deep, pH neutral to basic hydrothermal systems. We used in situ X-ray absorption spectroscopy (XAS) diamond-anvil cell experiments to determine Zn(II) speciation in a 1 m NaHS + 0.2 m HCl solution in contact with sphalerite. XANES data indicate that Zn coordinates to oxy/hydroxyl/chloride ligands from room temperature up to and including 200 °C, and then at higher temperatures ( $\geq$ 300 °C) and pressures ( $\geq$ 2 kbar) it changes to complexing with sulfur. Our data confirm that bisulfide complexes become increasingly important in neutral-alkaline solutions at high pressure and temperature, due to an increase in sulfur solubility and to favorable entropy contributions for bisulfide vs. chloride complexes.

Keywords: Zinc, sulfur, chloride, hydrothermal, high temperature and pressure