

Dissociation constants for HCl_(aq) and H₂S_(aq) in hydrothermal fluids by *ab initio* molecular dynamics simulations

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HCl and H₂S are two of the most significant volatiles in the Earth's crust. It is well established that chloride (Cl⁻) and bisulfide (HS⁻) play important roles in transporting metals (e.g., Cu, Au, Zn) in hydrothermal fluids. Thus, the thermodynamic properties of HCl and H₂S in aqueous solutions over a wide range of temperature and pressure are crucial for the understanding and numerical modelling of metal transport and deposition in hydrothermal fluids; however, significant discrepancies exist in the dissociation constants for HCl_(aq) and H₂S_(aq) determined from various experimental studies. For example, there is up to 5 orders of magnitude difference in *pK_a* values for HCl_(aq) in the literature (Pokrovskii, 1999). Here we conducted *ab initio* molecular dynamics (MD) simulations to calculate the *pK_a* values for HCl_(aq) and H₂S_(aq) in hydrothermal fluids, and constructed activity-activity diagrams of the solubility gradients of gold, copper and zinc minerals using the new properties.

Dissociation constants for HCl_(aq) and H₂S_(aq) at 25-350 °C were calculated by performing series of distance-constrained *ab initio* MD simulations using CPMD as described by Mei et al. (2013, 2015, 2016). The free energies of the HCl_(aq) and H₂S_(aq) dissociation reactions were obtained by thermodynamic integration. This computational study provides an independent check that helps to resolve the discrepancies of the dissociation constants for HCl_(aq) and H₂S_(aq) from different experimental studies, and provides new data for these important species in the hydrothermal fluids beyond experimental conditions.

References:

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