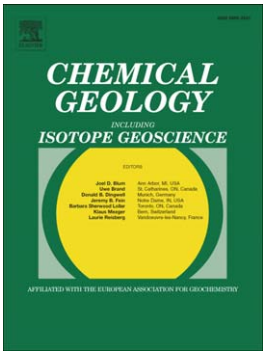

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Equilibrium isotopic fractionation between aqueous Zn and minerals from first-principles calculations

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Abstract

Theoretical mineral-solution equilibrium isotopic fractionation can contribute to the interpretation of Zn isotopic compositions. In this study, we investigate equilibrium isotopic fractionation properties of hexaaquo zinc complex, a major Zn aqueous species, using first-principles molecular dynamics (FPMD) based on density functional theory (DFT). Pentaaquo and tetraaquo zinc complexes, which can be relevant for specific mechanisms such as adsorption on mineral surfaces, are also considered. This approach takes into account both configurational and solvation effects that are less easily accounted for in molecular cluster models. The logarithmic value of the reduced partition function ratio of aqueous Zn ($\ln \beta$ ^{66}Zn/^{64}Zn) is 2.86 ± 0.04‰ at 295 K, while the same computational approach gave $\ln \beta$ ^{66}Zn/^{64}Zn in the range $2.2 - 4.1$‰ for various Zn-bearing minerals. For example, calculations predict at 295 K, equilibrium fractionations between mineral and aqueous Zn of -0.46‰ for primary zinc sulfide sphalerite and of -0.20‰ and +0.34‰ for secondary phases gunningite and hydrozincite, respectively. Molecular clusters are also modelled, predicting isotopically heavier Zn with respect to related FPMD models ($\ln \beta$ increases by 0.09 to 0.23‰). These values are small but significant in the Zn isotopic system and supports the idea that a proper description of the dynamics of the system and the solvation effect are required for a reliable prediction of the isotopic properties of solvated ions.

Keywords: Isotopic fractionation, aqueous zinc, mineral-solution fractionation, DFT, ab initio
2010 MSC: 00-01, 99-00

1. INTRODUCTION

Numerous studies have focused on Zn because of the anthropic footprint on Zn biogeochemical cycle (Rauch, 2010) and its important biological role (Albarède et al., 2017, and references therein). Our knowledge of global cycle of heavy metals depends on our ability in studying their mobility and their bioavailability.

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