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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). Pentaquo and tetraquo 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 ($\ln \beta^{66\text{Zn}/64\text{Zn}}$) is $2.86 \pm 0.04\text{‰}$ at 295 K, while the same computational approach gave $\ln \beta^{66\text{Zn}/64\text{Zn}}$ in the range $2.2 - 4.1\text{‰}$ 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 $+0.34\text{‰}$ 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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A key parameter controlling both of them is the chemical speciation in turn controlled by environmental conditions such as temperature, pH, the presence and nature of inorganic and organic phases. Recent advances in the measurement of non-traditional isotopes have provided new insights in the biogeochemical cycling of Zn (for reviews, see Cloquet et al., 2008; Moynier et al., 2017). The sensitivity of isotopic fractionation to crystal-chemistry and modifications of its atomic-scale environment allows to probe the involved molecular mechanisms (e.g. Pokrovsky et al., 2005; Juillot et al., 2008; Fujii et al., 2010; Black et al., 2011; Fujii et al., 2011; Fujii & Albarède, 2012; Fujii et al., 2014; Bryan et al., 2015; Guinoiseau et al., 2016; Dong & Wasylenki, 2016; Ducher et al., 2016).

At Earth’s surface, seawater and freshwater constitute together the second largest reservoir of Zn after soils and before the anthropic reservoir (Rauch & Pacyna, 2009). A particularly relevant Zn species in aqueous media is the free form of Zn also referred to as aqueous Zn i.e. Zn^{2+} solvated by water molecules. It is not only the most mobile, but also the most abundant Zn species in seawater and organic matter-free freshwater (Albarède, 2004, and references therein) and the most bioavailable form according to the free-ion activity model (Morel, 1983; Campbell, 1995). van Dijk et al. (2017) emphasised on the importance of aqueous Zn by suggesting that it could be the prevalent species during the formation of foraminiferal calcite rather than carbonated ones such as ZnCO_3 . Alternatively, Zn adsorption experiments onto calcite of Dong & Wasylenki (2016) suggested that the observed isotopic fractionation was driven by either a change of coordination number at the calcite surface or the adsorption of ZnCO_3 species.

Isotopic fractionation properties of well-identified Zn species in water are difficult to determine by experiment and measured isotopic fractionation values are often discussed in the light of theoretical studies of Zn isotope fractionation (Fujii et al., 2010; Black et al., 2011; Fujii et al., 2011, 2014). The theoretical results are affected by the assumptions made to model aqueous Zn species. The most preferred theoretical framework in the case of Zn isotope fractionation at equilibrium is density functional theory (DFT). Within this framework Zn species have been modelled as molecular clusters with one or two solvation shells around a Zn atom (Fujii et al., 2010; Black et al., 2011; Fujii et al., 2011, 2014). Such modelling is computationally cost-effective but the optimisation of the structures leads to static configurations, likely differing from those occurring at finite temperature. In addition, the treatment of solvation effects is often restricted to the use of polarised continuum models. Furthermore, these cluster-based theoretical studies of dissolved and complexed Zn species in water have not considered solid phases, making it difficult to derive of Zn isotope fractionation properties between solids and aqueous solutions. These difficulties have been pointed out in previous studies such as Rustad et al. (2010) in which isotopic properties of Mg, Ca and Fe were investigated.

In this study, we investigate the isotope fractionation properties of aqueous Zn at equilibrium using DFT-based FPMD simulations including dynamical and solvation effects, following an approach similar to that previously used by Pinilla et al. (2015) and Dupuis et al. (2015). Based on the previous study of Zn-bearing minerals (Ducher et al., 2016), these new results allows us to present theoretical mineral-solution

Figure 1: Snapshots of modelled aqueous Zn complexes. From left to right: FPMD model with one Zn and 64 H₂O, single solvation shell Zn01 molecular cluster model (Zn[H₂O]₆)²⁺ and double solvation shell Zn05 molecular cluster model (Zn[H₂O]₁₈)²⁺.

Zn isotope fractionations at equilibrium in which both the solid and aqueous solutions properties have been computed using the same framework.

2. METHODS

2.1. Equilibrium isotopic fractionation factors

Zn has five stable isotopes: ⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn, ⁶⁸Zn, ⁷⁰Zn, with abundances of 48.6 %, 27.9 %, 4.1 %, 18.8 % and 0.6 % respectively (Sansonetti & Martin, 2005). In this study, we focus on the ratio of the two most abundant Zn isotopes, i.e. ⁶⁶Zn/⁶⁴Zn. Equilibrium isotopic properties of an element in a given system are determined by the calculation of the reduced partition function ratio also called β -factor. Assuming that equilibrium mass-dependent isotopic fractionation arises mainly from the vibrational motions of atoms and in the harmonic approximation, the β -factor calculation requires only the knowledge of harmonic vibrational frequencies ν'_i and ν_i of the lightest and heaviest isotopologues respectively (Bigeleisen & Mayer, 1947; Blanchard et al., 2017):

$$\beta = \prod_{i=3}^{3N_{at}} \frac{\nu_i}{\nu'_i} \frac{\exp(-h\nu_i/2k_B T)}{1 - \exp(-h\nu_i/k_B T)} \frac{1 - \exp(-h\nu'_i/k_B T)}{\exp(-h\nu'_i/2k_B T)} \quad (1)$$

where k_B is the Boltzmann constant, h is the Planck constant, T is the temperature and N_{at} is the number of atoms in the computational-cell. Vibrational frequency calculations are performed at the centre of the Brillouin zone and thus, the branch index i starts at 3. The formula is given here for a system containing only one Zn atom. As the calculated β -factors are very close to 1, they will be presented as logarithmic quantities ($\ln \beta$) expressed in permil (‰).

2.2. Description of aqueous Zn in FPMD and molecular cluster approaches

2.2.1. FPMD approach

To ensure an acceptable sampling of Zn configurational disorder in solution, we perform DFT-based Born-Oppenheimer type first-principles molecular dynamics simulations. The simulation cell contains one Zn atom

and 64 water molecules (Figure 1). A uniform background charge is applied to compensate for Zn^{2+} positive charge. The cell-parameter of the cubic box is set at $12.65 \text{ \AA}$, so as to reproduce the experimental density of 1.0 kg/m^3 found at room-temperature. The simulation is performed in the NVT thermodynamic ensemble with the temperature fixed at 300 K and controlled by a Berendsen thermostat (Berendsen et al., 1984) with a coupling time constant of 0.3 ps. The time step used for the integration of equation of motions to evolve the ionic positions is 0.97 fs. It is chosen such as the shortest vibrational period in the system (OH stretching vibrations with a period of 9 – 10 fs) is about 10 times larger. This kind of FPMD trajectories generate several thousands of molecular configurations. To keep the computation time within realistic limits, two approximations are then used to compute the Zn β -factors: (i) only 20 snapshots from the FPMD trajectories are considered, as previously proposed in previous molecular dynamics studies of isotopic fractionation in aqueous solution (e.g. Kowalski & Jahn, 2011; Kowalski et al., 2013; Pinilla et al., 2015; Dupuis et al., 2015), (ii) after a proper checking based on a full calculation of vibrational frequencies and use of equation 1, the β -factors are determined using the one-to-one relation between Zn β -factors and interatomic force constants (F) previously reported by Ducher et al. (2016).

2.2.2. Molecular cluster approach

So far, studies focusing on the calculation of Zn isotope fractionation have modelled aqueous Zn only as molecular clusters (Fujii et al., 2010, 2011; Fujii & Albarède, 2012; Fujii et al., 2014; Black et al., 2011). In order to benchmark our FPMD results, we perform such calculations on five Zn molecular clusters. These molecular clusters were taken from Black et al. (2011) and have a variable number of water molecules (Figure 1). In two of these models, namely Zn01 and Zn02, Zn atom has only a single solvation shell while in the three others (Zn03, Zn04 and Zn05), Zn atom has a double solvation shell. The molecular clusters are isolated in a cubic box with a cell parameter of $31.75 \text{ \AA}$, which is large enough to avoid the interaction of charged images with their periodic neighbours. In addition, Martyna-Tuckerman corrections (Martyna & Tuckerman, 1999) are enabled to further isolate the molecule in the simulation box. Before isotopic property calculation, the ionic positions are relaxed using DFT. As we did for molecular dynamics simulation cell, a uniform negative background charge is applied.

2.3. Computational details

Molecular dynamics simulations, atomic relaxations and vibrational frequency calculations are carried out using PWSCF and PHONON codes that are included in the DFT-based Quantum ESPRESSO suite of codes (Giannozzi et al., 2009), which uses plane-waves, pseudopotentials and periodic boundary conditions. We use for the exchange-correlation functional the Perdew-Burke-Ernzerhof (PBE) parameterisation (Perdew et al., 1996) of the generalised gradient approximation (GGA) functional and the vdW-DF2 functional (Lee et al., 2010). The latter functional provides a better description than GGA of van der Waals interactions

Figure 2: Evolution of Zn coordination number (top panels) and calculated interatomic force constants of selected snapshots (bottom panels) from (a) vdW-DF2 and (b) GGA FPMD trajectories.

that are essential in this system (Ducher et al., 2017). Molecular dynamics simulations are performed with both functionals while molecular cluster calculations are done with GGA-PBE functional. The ionic cores of Zn, O and H are described by ultrasoft pseudopotentials from the GBRV library (Garritty et al., 2014) as in Ducher et al. (2016, 2017). The cut-off energies for wave-functions and charge-density expansions in finite basis-sets are fixed at 50 Ry and 450 Ry respectively. These values are lower than those used by Ducher et al. (2016), i.e. 80 Ry and 720 Ry, but isotopic properties are almost unaffected. For example, only a decrease of $\ln \beta$ $^{66}\text{Zn}/^{64}\text{Zn}$ by 0.06 ‰ at 295 K is observed on a $(\text{Zn}[\text{H}_2\text{O}]_6)^{2+}$ molecular cluster, when the cut-off energies are increased. The Brillouin zone sampling for electronic integration is restricted to the Γ -point. The vibrational frequencies are calculated after diagonalisation of the dynamical matrices for the two Zn isotope masses (^{64}Zn and ^{66}Zn).

3. RESULTS

3.1. Structural properties of aqueous Zn

Isotopic fractionation property calculations rely on vibrational properties that in turn, depend on the structure of the system under consideration. Consequently, we check the structural properties of our models by comparing them with experimental results.

3.1.1. Molecular dynamics models

Experimentally, hexaaquo-zinc complex is the main species of Zn when the first coordination sphere of Zn is composed of water molecules only (e.g. Kuzmin et al., 1997, and references therein). In our FPMD trajectories, with both GGA-PBE and vdW-DF2 functionals, hexaaquo-zinc complexes are observed (Fig 1 and 2). However, with GGA-PBE functional, in addition to these complexes, pentaquo and tetraquo complexes were also observed successively (Ducher et al., 2017). This is suggested to be due to a poor description of van der Waals interactions by GGA-PBE. VdW-DF2 functional remedies this problem

by providing a better description of such interactions and restores the expected energetic order between Zn coordination states. Although, the energetics of the system is functional dependent, the structural properties of a given species, are almost identical. Bond lengths between the element of interest and its neighbours is an important crystal-chemical parameter controlling isotopic properties (Schauble, 2011; Kowalski & Jahn, 2011; Kowalski et al., 2013; Méheut & Schauble, 2014) through its impact on Zn interatomic force constant as shown by Ducher et al. (2016). The average Zn-O bond length of hexaaquo complexes from GGA-PBE and vdW-DF2 FPMD trajectories are very similar (2.17 Å and 2.19 Å respectively). These values are overestimated with respect to experimental values observed in this system that fall in the range of [2.06; 2.15] Å (Kuzmin et al., 1997; Maeda et al., 1996). This effect is due to the GGA-PBE and vdW-DF2 exchange-correlation functionals which are known to overestimate bond lengths (e.g. Hamada & Otani, 2010; Hamada, 2014; Ducher et al., 2016). Calculated EXAFS spectra of hexaaquo complexes in FPMD trajectories are fully consistent with the experimental spectra (Cauët et al., 2010; Ducher et al., 2017) showing that hexaaquo-zinc complexes of DFT-based FPMD simulations are very similar to those observed in the experiments.

3.1.2. Zn molecular clusters

In standard DFT calculations, the hexaaquo zinc complex is stable after atomic position relaxation with GGA-PBE functional. In the optimised structures, the average Zn-O bond length is 2.12 Å for both Zn01 and Zn02 models, which is lower than FPMD values. This value matches with the 2.13 Å found using B3LYP functional on these molecular clusters by Fujii et al. (2010) and by Black et al. (2011). With 18 H₂O, the average bond lengths are 2.14 Å, 2.13 Å and 2.12 Å in the Zn03, Zn04 and Zn05 models respectively (Zn03 model being the one with the most scattered Zn-O bond lengths: 2.08, 2 × 2.13, 2.14, 2.15 and 2.22 Å). These values are again smaller than the FPMD values.

3.2. Reduced partition function ratios of aqueous Zn

3.2.1. FPMD results

We first compare the isotopic fractionation properties of hexaaquo Zn obtained with the PBE and vdW-DF2 functionals. As described in Section 2, we extract 20 snapshots uniformly spaced in time as shown in Figure 2. On each snapshot, all atomic positions are relaxed and the force constant F is calculated. The snapshot having the closest F value to the average F is then selected to compute the Zn β -factor from the full sets of vibrational frequencies (Eq 1) for both the GGA-PBE and vdW-DF2 trajectories (Table 1). Two other snapshots corresponding to the lowest and highest F values were considered (Table 1). According to these calculations, at the temperature of the FPMD trajectories (300 K), the average $\ln \beta^{66\text{Zn}/64\text{Zn}}$ of GGA-PBE and vdW-DF2 trajectories are 2.77‰ and 2.76‰ respectively. This small difference is in

Table 1: Reduced partition function ratios ($\ln \beta$ $^{66}\text{Zn}/^{64}\text{Zn}$ in ‰) of Zn in selected snapshots from FPMD trajectories performed with GGA-PBE and vdW-DF2 functionals and in molecular clusters on which full vibrational frequency calculations are performed. "average", "minimum" and "maximum" correspond to snapshots having the average, the lowest and the highest Zn interatomic force constant F respectively, which is a measure of Zn-O bond strength.

			$\ln \beta$ $^{66}\text{Zn}/^{64}\text{Zn}$				
			273 K	295 K	300 K	323 K	373 K
FPMD	GGA-PBE	average ($F = 1.72 \text{ Ry}/\text{\AA}^2$)	3.31	2.86	2.77	2.40	1.82
		minimum ($F = 1.68 \text{ Ry}/\text{\AA}^2$)	3.25	2.80	2.71	2.36	1.79
		maximum ($F = 1.81 \text{ Ry}/\text{\AA}^2$)	3.49	3.01	2.92	2.53	1.92
	vdW-DF2	average ($F = 1.68 \text{ Ry}/\text{\AA}^2$)	3.31	2.85	2.76	2.40	1.82
		minimum ($F = 1.54 \text{ Ry}/\text{\AA}^2$)	3.02	2.61	2.53	2.19	1.66
		maximum ($F = 1.81 \text{ Ry}/\text{\AA}^2$)	3.50	3.03	2.93	2.55	1.93
Molecular cluster	GGA-PBE	Zn01 (C_1 symm.)	3.50	3.02	2.92	2.54	1.92
		Zn02 (T_h symm.)	3.70	3.19	3.09	2.68	2.03
		Zn03 (C_1 symm.)	3.49	3.01	2.91	2.53	1.92
		Zn04 (T symm.)	3.42	2.95	2.85	2.48	1.87
		Zn05 (C_3 symm.)	3.50	3.02	2.93	2.54	1.92

line with structural properties, which suggested that both functionals predict almost the same aqueous Zn structure. In the following, we will mostly focus on the GGA-PBE FPMD results.

We now relate the β -factor values obtained from a full calculation of vibrational frequencies to the corresponding force constants (Figure 3). A linear correlation between these two quantities has been observed by Ducher et al. (2016) for a series of Zn-bearing minerals. The present results indicate that the same relation still holds for aqueous Zn using either the GGA-PBE or the vdW-DF2 functionals (Figure 3). This means that an average β -factor can be obtained by considering an average of the force constants determined on the 20 snapshots. It turns out that the snapshot displaying a Zn interatomic force constant closest to the average value should also display the average β -factor value. In fact, using the linear correlation (Figure 3) and the average force constant of the 20 GGA-PBE snapshots, the average $\ln \beta$ $^{66}\text{Zn}/^{64}\text{Zn}$ of aqueous Zn is 2.88 ‰ at 295 K, which is very close to the value obtained with a full calculation on the "average" snapshot (2.86 ‰). This very small difference suggests that in the future studies, if the same computational techniques and parameters are used, only the Zn interatomic force constant calculation would be required to derive β -factors without performing vibrational frequency calculation. Using linear fits of the data published on minerals (Table 2), β -factors are also calculated at other temperatures (Table 3). The error bars $\Delta \ln \beta$ on $\ln \beta$ at a given temperature are calculated using standard error propagation: $\Delta \ln \beta = g'(F)\delta F$ with $g'(F)$ the slope of the linear correlation function at a given temperature (Table 2) and δF the error bar on F given in Table 3. For instance, at 295 K, the expression of the linear correlation is $\ln \beta = 1.5767F + 0.1640$, which leads to an error bar of 0.04 ‰.

The length of the vdW-DF2 (24 ps) and GGA-PBE (5.5 ps) trajectories used in the calculation of the

Figure 3: Aqueous Zn $\ln \beta^{66}\text{Zn}/^{64}\text{Zn}$ from FPMD GGA-PBE and vdW-DF2 trajectories from Table 1 at 295 K reported as a function of Zn interatomic force constant F . The same quantities for Zn in minerals as well as the linear correlation ($\ln \beta^{66}\text{Zn}/^{64}\text{Zn}(\text{‰}) = 1.5767F + 0.1640$) from Ducher et al. (2016) are also reported.

Table 2: Linear fits calculated from Ducher et al. (2016) data, of type: $aF + b$ of $\ln \beta$ (in ‰) when plotted as a function of Zn interatomic force constant F (in $\text{Ry}/\text{\AA}^2$) for Zn-bearing minerals. These linear correlations are used to determine β -factors when the full frequency calculations are not performed.

	a ($\text{\AA}^2/\text{Ry}$)	b
273 K	1.8125	0.2233
295 K	1.5767	0.1640
323 K	1.3367	0.1124
373 K	1.0261	0.0553

force constants of hexaaquo zinc complexes are different. In the vdW-DF2 trajectory, snapshots are extracted every 1,300 FPMD steps while in the GGA-PBE trajectory, they are extracted every 300 steps. To rule out any sampling length related effects on F , we have also calculated the average value of F given by the portion of vdW-DF2 trajectory between 6 and 11.5 ps (still with 20 snapshots). The whole trajectory and a portion of it give identical F values with $1.68 \pm 0.03 \text{ Ry}/\text{\AA}^2$ and $1.67 \pm 0.03 \text{ Ry}/\text{\AA}^2$ respectively. This shows that short FPMD trajectories of about 5 ps (after equilibration) are already enough for isotopic property calculations.

In GGA-PBE trajectories, in addition to hexaaquo complexes, tetraaquo and pentaquo ones are also observed. The knowledge of the isotopic properties of these complexes are useful as they could be relevant during the adsorption of aqueous Zn on mineral surfaces. Using the correlation mentioned previously, β -factors for tetraaquo and pentaquo complexes are determined (Table 3). According to these values, at 295 K, average $\ln \beta$ difference between hexaaquo and tetraaquo is -1.30 ‰ and between hexaaquo and pentaquo

Table 3: Average Zn interatomic force constants F calculated for GGA-PBE and vdW-DF2 trajectories from 20 FPMD snapshots (in $\text{Ry}/\text{\AA}^2$). The confidence level on average interatomic force constants is 95 % and the confidence interval is calculated assuming a Student's t-distribution. One standard deviation (1 StDev) of the Zn F is also given. "no relax", "relax Zn" and "relax all" refer to no atomic position relaxation, the relaxation of only Zn position and the relaxation of all positions respectively. For each relaxation procedure, $\ln \beta^{66}\text{Zn}/^{64}\text{Zn}$ are reported using the linear fits given in Table 2.

		F	1 StDev	$\ln \beta$ at 273 K	$\ln \beta$ at 295 K	$\ln \beta$ at 323 K	$\ln \beta$ at 373 K
GGA-PBE (5.5 ps) (hexaaquo zinc)	relax all	1.72 ± 0.02	0.04	3.32 ± 0.04	2.86 ± 0.04	2.41 ± 0.03	1.82 ± 0.03
	relax Zn	1.78 ± 0.11	0.23	3.45 ± 0.20	2.97 ± 0.18	2.49 ± 0.15	1.88 ± 0.12
	no relax	1.84 ± 0.12	0.24	3.56 ± 0.22	3.07 ± 0.19	2.57 ± 0.16	1.94 ± 0.13
GGA-PBE (3.8 ps) (pentaquo zinc)	relax all	2.05 ± 0.02	0.05	3.94 ± 0.04	3.40 ± 0.04	2.85 ± 0.03	2.16 ± 0.02
	relax Zn	1.98 ± 0.10	0.21	3.81 ± 0.18	3.28 ± 0.16	2.76 ± 0.13	2.09 ± 0.10
	no relax	2.09 ± 0.11	0.22	4.01 ± 0.19	3.46 ± 0.16	2.90 ± 0.14	2.20 ± 0.11
GGA-PBE (14.3 ps) (tetraquo zinc)	relax all	2.54 ± 0.02	0.05	4.82 ± 0.04	4.16 ± 0.03	3.50 ± 0.03	2.66 ± 0.02
	relax Zn	2.54 ± 0.13	0.27	4.82 ± 0.23	4.16 ± 0.20	3.50 ± 0.17	2.66 ± 0.13
	no relax	2.57 ± 0.12	0.26	4.88 ± 0.22	4.22 ± 0.19	3.55 ± 0.16	2.69 ± 0.13
vdW-DF2 (24 ps)	relax all	1.68 ± 0.03	0.06	3.29 ± 0.06	2.85 ± 0.05	2.38 ± 0.05	1.81 ± 0.04
	relax Zn	1.67 ± 0.08	0.16	3.25 ± 0.15	2.80 ± 0.13	2.34 ± 0.11	1.77 ± 0.09
	no relax	1.72 ± 0.09	0.18	3.34 ± 0.17	2.88 ± 0.15	2.41 ± 0.13	1.82 ± 0.10

is -0.54% .

3.2.2. Molecular cluster results

On each of the five Zn molecular clusters, β -factor are calculated after full vibrational frequency calculations. $\ln \beta^{66}\text{Zn}/^{64}\text{Zn}$ at 295 K are found to be scattered around 3% with a maximum difference between the lowest and highest value of 0.24% . Going from models with a single solvation shell to those having a double solvation shell, $\ln \beta^{66}\text{Zn}/^{64}\text{Zn}$ either remains identical or decreases depending on the models. Between Zn01 and Zn03 having the same symmetry (C_1), the decrease at 295 K is only 0.01% while between Zn02 (T_h symmetry) and Zn04 (T symmetry), it is 0.24% . $\ln \beta^{66}\text{Zn}/^{64}\text{Zn}$ calculated in molecular clusters are also larger than FPMD values by at least 0.09% and at most by 0.23% at 295 K.

4. DISCUSSION

4.1. Temperature extrapolation of β -factors

Temperature extrapolation of β -factors using Eq 1 is a common approximation for the calculation of isotopic properties of minerals in which one assumes that the structure does not change much with temperature. In liquids however, this assumption should be used with care as these systems are more sensitive to thermal effects than solids. FPMD studies performed by Liu et al. (2011) and Mei et al. (2015), investigated the coordination of aqueous Zn at hydrothermal conditions. They observed the destabilisation of the hexaaquo complex and the stabilisation of tetraquo complexes. However, their calculations were performed using GGA functionals, which give incorrectly destabilise hexaaquo zinc complex (Ducher et al.,

200 2017). An important point to notice in these GGA simulations is that hexaaquo state is already metastable at room temperature and becomes completely unstable at high temperature. With an approach including van der Waals forces in the modelling, hexaaquo state is the most stable one with respect to tetraaquo and pentaquo states (Ducher et al., 2017). A qualitative estimation shows that an increase of the temperature up to 373 K would be associated with 0.6 kJ mol^{-1} energy increase, which is much smaller than the energy barrier between the aqueous Zn states. A change of the coordination state is thus unlikely on this range indicating that properties of the FPMD trajectories at 300 K can be extrapolated up to 373 K. Consistently, Pinilla et al. (2015) showed in the case of Mg isotope fractionation that the temperature extrapolation gives identical results as compared to FPMD calculation performed at different temperatures up to 400 K. Therefore, we use the 273-373 K temperature range to perform polynomial fit of type $ax^2 + bx$ with $x = 10^6/T^2$, of calculated $\ln \beta^{66\text{Zn}/64\text{Zn}}$ using Eq 1. It gives coefficients values of $a = -1.08 \times 10^{-3} \text{ K}^4$ and $b = 0.2613 \text{ K}^2$. For all other β -factors based on full frequency calculations, polynomial fit parameters are reported in Table S1 of Supplementary Information.

4.2. Effect of atomic position relaxation on reduced partition function ratios of aqueous Zn

In Section 3.2.1, average aqueous Zn β -factors are calculated after relaxation of all atomic positions. The relaxation of all positions is motivated by the requirement of Eq 1 to use only harmonic frequencies. If snapshots without relaxation or with only the relaxation of Zn position are used to perform vibrational frequency calculations, an important number of "negative frequencies" appear ($\sim 10\%$ of total frequencies). The absolute values of these frequencies fall between 0 cm^{-1} and 700 cm^{-1} that is the range in which vibrational modes contribute the most to aqueous Zn β -factor (more than 90%). In fact, β -factors calculated ignoring these negative frequencies are out of the correlation line of Figure 3 (Figure S1 of Supplementary Information). However, we have noticed that even when Zn atoms are out of their equilibrium positions, they are still on their harmonic potential surface thanks to their relatively large atomic mass. Thus, Zn interatomic force constants calculated on unrelaxed snapshots can be used to derive β -factors (using the correlation of Figure 3) but full frequency calculations should not be performed as oxygen (and hydrogen) atoms are likely out of the harmonic potential surface when atomic positions are out of equilibrium. For the two other relaxation procedures ("no relax" and "relax Zn") β -factors are derived at various temperatures (Table 3) using the linear correlations between F and $\ln \beta$ at various temperatures.

Pinilla et al. (2015) suggested that the relaxation of all positions could remove some of the thermal disorder leading to a decrease of average value and narrowing of standard deviation of F with the relaxation. A similar narrowing is also observed in this work, with F calculated after the full relaxation of atomic positions having the smallest standard deviation (Table 3.). However, the average F value with relaxation of all positions is not always the smallest when compared to the two other relaxation procedures. For instance, the smallest average F is obtained by relaxing only Zn position with vdW-DF2. Therefore, the

lower average F value of the fully relaxed model with respect to the values without relaxation and with relaxation restricted to the Zn position might be a statistical effect and could disappear with an increased sampling statistics.

4.3. Comparison with molecular cluster calculations

The previous studies on Zn isotope fractionation (Fujii et al., 2010, 2011, 2014; Black et al., 2011) have used codes that have a different numerical implementation of DFT than ours, which makes it difficult a straightforward comparison between their results and ours. Some variability in the calculated β -factors occurs depending on the nature and size of the basis-set used as it was shown by the study of Fujii et al. (2011) in which $\ln \beta$ variation of almost 1 ‰ was observed between the $6-311G(d)$ and $6-31+G(d,p)$ basis-sets at room temperature. In order to compare molecular dynamics and molecular cluster approaches, we modelled aqueous Zn as small molecular clusters with one or two solvation shells within the same computational method as used for the FPMD runs, i.e. planewave basis and periodic boundary conditions. This allows to discuss in more details the effects of solvation and structural disorder on Zn isotope fractionation.

Molecular cluster calculations are performed by fully relaxing the atomic positions at 0 K. Therefore, the comparison of FPMD results obtained with a full relaxation of atomic positions at 0 K ("relax all") with molecular cluster ones shows that all five molecular cluster models overestimate $\ln \beta$ by 0.09 ‰ to 0.23 ‰ (Table 4). To investigate the origin of this difference, two new models are made from the relaxed average FPMD snapshot. In the new models, only one Zn atom with either one solvation shell (FPMD cluster $(\text{Zn}[\text{H}_2\text{O}]_6)^{2+}$) or two solvation shells (FPMD cluster $(\text{Zn}[\text{H}_2\text{O}]_{18})^{2+}$) are extracted from the FPMD configuration $(\text{Zn}[\text{H}_2\text{O}]_{64})^{2+}$. The β -factors are then obtained either after a relaxation of atomic positions or at the initial FPMD positions. With only the first solvation shell kept, the six Zn-O bond lengths after relaxation are equal (2.12 Å), while without relaxation the average length is 2.15 Å with a standard deviation of 0.08 Å. The structural disorder is thus removed by the relaxation of atomic positions when only one solvation shell is present. For the model with unrelaxed atomic positions, the value of $\ln \beta$ at 295 K is 2.99 ‰ whereas the shortest Zn-O bond length of the relaxed model leads to an increase of $\ln \beta$ to 3.03 ‰. This illustrates the contribution of the distortion of the first solvation shell to isotopic fractionation properties. Both $\ln \beta$ values are larger than the FPMD value of 2.86 ‰, a difference due to the lack of farther solvation shells. When two solvation shells are considered the magnitude of the variation is much more limited and a $\ln \beta$ of 2.88 ‰ is calculated that is within the error bar of the FPMD value. In this case, the relaxation of atomic positions has no effect on the average Zn-O bond length, which is the same as the unrelaxed value with however a smaller dispersion of individual bond lengths (0.04 Å) with respect to the unrelaxed configuration (0.08 Å). The $\ln \beta$ difference between unrelaxed and relaxed configurations is only 0.06 ‰ (Table 4). The impact of β -factors of the temperature-dependent distortion of the Zn coordination shell is comparatively less important than that of solvation effects. Thus, molecular cluster models with a single solvation shell

Table 4: Calculated $\ln \beta^{66\text{Zn}/^{64}\text{Zn}}$ at 295 K (in %) from molecular cluster models with one (Zn01 and Zn02) or two (Zn03, Zn04 and Zn05) solvation shells, molecular dynamics model (FPMD $\text{Zn}[\text{H}_2\text{O}]_{64}^{2+}$ and cluster models made from the molecular dynamics model (FPMD cluster $\text{Zn}[\text{H}_2\text{O}]_6^{2+}$ and FPMD cluster $\text{Zn}[\text{H}_2\text{O}]_{18}^{2+}$). Our results are compared with Black et al. (2011) study in which two basis-set were used with B3LYP functional. For Black et al. (2011) study, the top values in each row correspond to *aug-cc-pVDZ* basis-set for all atoms while the bottom values correspond to *LANL2DZ* basis-set for Zn and *6-31G** for O and H atoms. Fujii et al. (2011) also studied aqueous Zn with B3LYP functional and *6-311+G(d,p)* basis-set and their results are reported for comparison.

Model	Chemical formula	Symmetry	This study	Black et al.	Fujii et al.
Zn01	$(\text{Zn}[\text{H}_2\text{O}]_6)^{2+}$	C_1	3.02	3.11 3.82	
Zn02	$(\text{Zn}[\text{H}_2\text{O}]_6)^{2+}$	T_h	3.19	3.21 3.82	3.33
Zn03	$(\text{Zn}[\text{H}_2\text{O}]_{18})^{2+}$	C_1	3.01	3.23 3.93	3.64
Zn04	$(\text{Zn}[\text{H}_2\text{O}]_{18})^{2+}$	T	2.95	3.17 3.89	
Zn05	$(\text{Zn}[\text{H}_2\text{O}]_{18})^{2+}$	C_3	3.02	3.36 3.89	
FPMD	$(\text{Zn}[\text{H}_2\text{O}]_{64})^{2+}$	C_1	2.86 ± 0.04		
FPMD cluster (positions relaxed)	$(\text{Zn}[\text{H}_2\text{O}]_6)^{2+}$	C_1	3.03		
FPMD cluster (positions not relaxed)	$(\text{Zn}[\text{H}_2\text{O}]_6)^{2+}$	C_1	2.99		
FPMD cluster (positions relaxed)	$(\text{Zn}[\text{H}_2\text{O}]_{18})^{2+}$	C_1	2.82		
FPMD cluster (positions not relaxed)	$(\text{Zn}[\text{H}_2\text{O}]_{18})^{2+}$	C_1	2.88		

(Zn01 and Zn02) hardly represent the average aqueous Zn molecular environment. In the molecular clusters with two solvation shells (Zn03, Zn04 and Zn05), the solvation effects are reasonably well captured but their β -factor is still different from the FPMD value. This indicates that further coordination shells should be considered to obtain a proper description of aqueous solutions with a cluster-based approach. We also notice a decrease of β -factors when the number of solvation shells is increased from one to two (Table 4). This observation is in line with quantum chemical calculations performed by Rustad et al. (2010) on Mg^{2+} , who also showed a β -factor decrease with increasing number of solvation shells.

4.4. Vibrational properties of hexaaquo zinc complexes

The isotopic fractionation of aqueous Zn is dominated by the vibrational properties of Zn-O bonds. In the case of hexaaquo-zinc complex with O_h symmetry, three vibrational modes ν_1 , ν_2 and ν_3 are expected with the first one corresponding to Raman-active symmetric stretching modes of Zn-O and the last one to infrared-active asymmetric stretching mode (Rudolph & Pye, 1999; Mink et al., 2003). The two experimental

Table 5: Vibrational frequencies of Raman active symmetric stretching ν_1 , asymmetric stretching ν_2 modes and infrared-active asymmetric stretching ν_3 mode. The calculated frequencies in our study are compared with DFT calculations from Black et al. (2011) and Fujii et al. (2011) and experimental values from Rudolph & Pye (1999) and Mink et al. (2003).

Reference	Model	ν_1	ν_2	ν_3
This study	Zn02 T_h symm	392	167	253 + HOH wagging 313 + HOH bending
	Zn04 T symm	352	267	330
	Zn05 C_3 symm	349 + HOH wagging	272	325 + HOH bending
		365 + HOH twisting		355 + HOH wagging
	MD ^a C_1 symm	392		357
Black et al. (2011)	Zn02 T_h symm	340	211	281
	Zn04 T symm	366	268	337
	Zn05 C_3 symm	359	264	335
Fujii et al. (2011)	$(\text{Zn}[\text{H}_2\text{O}]_6)^{2+}$ T_h symm	333	219	294
	$(\text{Zn}[\text{H}_2\text{O}]_{18})^{2+}$	380	298	362
Rudolph & Pye (1999)	Exp	390	270	365
Mink et al. (2003)		389	360	386

^a Model corresponding to the whole molecular dynamics simulation cell with 1 Zn and 64 H₂O. The ν_1 and ν_3 frequencies were computed using a partial dynamical matrix (see text). The ν_2 frequency could not be unambiguously identified.

studies provide consistent values for ν_1 mode ($\sim 390 \text{ cm}^{-1}$) and ν_3 mode ($365 - 386 \text{ cm}^{-1}$), with some uncertainties on absolute frequencies due to the broadness of absorption bands in solution (Table 5). On the other hand, these two studies disagree on the ν_2 -mode frequency (270 cm^{-1} versus 360 cm^{-1}). As already noted by Fujii et al. (2011), adding explicitly a second solvation shell to the molecular clusters improves the agreement between calculations and measurements (Table 5). Globally theoretical results from Fujii et al. (2011) and Black et al. (2011) support the assignment of Rudolph & Pye (1999), which was already based on a comparison with *ab initio* calculations. Present results are in line with previous ones. In the molecular clusters with two solvation shells, ν_1 , ν_2 and ν_3 modes appear at $349 - 365 \text{ cm}^{-1}$, $267 - 272 \text{ cm}^{-1}$ and $325 - 355 \text{ cm}^{-1}$, respectively, depending on the cluster symmetry and on which HOH vibrational mode they are coupled with. In the molecular dynamics model, the symmetry of the complex is reduced and the three modes are not easily identified because of significant vibrational coupling with the surrounding water molecules. In this case, the ν_1 and ν_3 modes can still be identified by diagonalising a partial dynamical matrix restricted to the 19 atoms of the $\text{Zn}[\text{H}_2\text{O}]_6^{2+}$ complex. The corresponding ν_1 and ν_3 frequencies are in excellent agreement with experimental observations of Rudolph & Pye (1999) (Table 5).

The contribution of vibrational modes to the Zn isotopic fractionation can be directly depicted from the FPMD trajectories (Figure 4). The importance of the second shell for a proper description of vibrational properties is evidenced by this analysis. When only one solvation shell is modelled, the vibrational modes that contribute to the β -factor have wavenumbers below 520 cm^{-1} . The HOH rocking modes that appear

Figure 4: Contribution of vibrational frequencies to the β -factor expressed as $\ln \beta ^{66}\text{Zn}/^{64}\text{Zn}$ (in ‰) at 295 K. The number of water molecules and crystallographic symmetry of each model are given in Table 4.

around 510 cm^{-1} make a contribution to $\ln \beta$ at 295 K of 0.6 ‰ due to the displacement of O atoms. Such an important effect is not observed with larger number of solvation shells. The contributions of vibrational modes of water molecules above 400 cm^{-1} are only around 0.2 ‰ to 0.3 ‰ to $\ln \beta$ at 295 K and they are spread over a broad range comprised between 400 cm^{-1} and 1000 cm^{-1} . Vibrational contributions to the β -factor between molecular cluster models with two solvation shells and FPMD model is almost identical up to 320 cm^{-1} . Between 320 cm^{-1} and 400 cm^{-1} , ν_1 and ν_3 modes contribute less to the β -factor in the FPMD model with 64 H_2O than in the cluster with two solvation shells (Zn03, Zn04 and Zn05). Although, these cluster models provide a better description of the vibrational properties, there is still a difference with the full FPMD model. However, the FPMD based cluster model with 18 H_2O displays almost the same contribution of vibrational modes to the β -factor than the full FPMD model, with only a small difference between 320 cm^{-1} and 400 cm^{-1} (Figure 4). This is consistent with their close β -factor values (Table 4). Therefore, a proper estimation of the average aqueous Zn β -factor can be provided by the average FPMD configuration in which only two solvation shells are kept.

4.5. Mineral-solution fractionation and geochemical implications

Isotopic fractionation properties of Zn-bearing minerals have been investigated by Ducher et al. (2016). As the numerical methods were the same as those used in the present study, β -factors of Zn in minerals can be compared with those of aqueous Zn calculated here (Figure 5). Compared with the broad range of mineral phases considered, aqueous Zn has the largest β -factor of the phases having 6-fold coordinated Zn only, i.e.

Figure 5: Temperature dependence of reduced partition function ratios (β -factors). Aqueous Zn β -factor with associated errorbars is given in black. Gray lines correspond to Zn β -factors in Zn-bearing minerals calculated by Ducher et al. (2016). The name of the phases are given by descending order of $\ln \beta$ at the right side of the plot.

smithsonite and gunningite (Figure 5). In thermodynamic equilibrium, smithsonite would be significantly depleted in ^{66}Zn with respect to the hexaaquo Zn complex (-0.56‰ at 295 K for smithsonite-solution). Aqueous Zn has also a β -factor larger than the Zn octahedral sites of adamite and hydrozincite (in these two minerals, Zn displays various coordination numbers). The Zn-O bond thus appears as relatively strong in the aqueous Zn complex. This is explained by the relatively weak interactions between the Zn first neighbours and farther water molecules, which results in a higher electrostatic charge on O atoms. We stress that this is not a general conclusion and for example, minerals in which Zn is present as trace in octahedral sites for example, could display larger Zn β -factors than aqueous Zn due to structural distortion of Zn crystal sites. Minerals in which Zn occupies a tetrahedral site (gahnite, hemimorphite, zincite, franklinite) or have two types of sites with different symmetry (hydrozincite, adamite) would be enriched in heavy Zn isotopes with respect to aqueous Zn (Figure 5). The largest positive fractionation between mineral among those calculated in Ducher et al. (2016) and solution is 1.19‰ at 295 K and obtained calculated between gahnite and aqueous Zn.

In Ducher et al. (2016), the aqueous Zn β -factor was roughly estimated from a small molecular cluster model. The present revised value leads to fractionations at 295 K, of -0.46‰ for sphalerite-solution and 0.34‰ for hydrozincite-solution. Although slightly larger, these values are in fair agreement with the experimental values of Veeramani et al. (2015), which are -0.30‰ and 0.18‰ respectively. In these experiments, Zn speciation in solution is uncertain but this comparison suggests that the isotopic equilibrium is attained

or nearly attained.

During oxidative weathering experiments of sphalerite-rich rocks, Fernandez & Borrok (2009) measured a $\Delta^{66}\text{Zn}_{\text{sphalerite-solution}}$ comprised between -0.2‰ to 0.0‰ . Sphalerite has one of the lowest β -factor among all investigated phases with $\ln \beta = 2.40\text{‰}$ at 295 K. The fractionation between sphalerite and aqueous Zn (-0.46‰) cannot explain the experimental value. However, the authors suggested that this value could represent the fractionation between sphalerite and the oxidation product of this mineral that could be Zn-sulfate. The Zn-sulfate gunningite has a $\ln \beta$ of 2.66‰ at 295 K. The fractionation between sphalerite and gunningite is therefore -0.26‰ which could be consistent with a slight enrichment in heavy isotopes of Zn of the oxidized sphalerite surface.

5. Conclusion

Using first-principles molecular dynamics based on density functional theory, we have calculated aqueous Zn isotopic properties. The average aqueous Zn β -factor has been calculated using an efficient sampling strategy based on the one-to-one relation between Zn interatomic force constant and β -factor, and using a single molecular dynamics snapshot that corresponds to the configuration having the average Zn interatomic force constant. Statistical error on $\ln \beta$ due to the sampling is also estimated using the same relation. At 295 K, $\ln \beta^{66}\text{Zn}/^{64}\text{Zn}$ is calculated to be $2.86 \pm 0.04\text{‰}$. We have investigated the validity of the molecular cluster approach. This approach gives overestimated β -factors for all models. The thorough investigation of single shell molecular cluster models lacking solvation effects show that they capture badly vibrational properties of aqueous Zn. The investigation of molecular cluster models with two solvation shells shows that they describe reasonably well the solvation effects but they do not represent the average Zn molecular configuration. Our results indicate that thermodynamic equilibrium can lead to Zn isotope fractionation ranging from -0.56‰ to 1.2‰ at 295 K between mineral phases and hexaaquo zinc complexes. The isotopic fractionation is large especially when a coordination number change occurs. β -factors presented here and in Ducher et al. (2016) provide a sound basis for interpreting mineral-solution Zn isotope fractionations.

Theoretical studies investigating basis-set effects on Zn molecular clusters with two solvation shells would be needed as we found contradicting results with previous studies (Black et al., 2011; Fujii et al., 2011). At the same time, theoretical studies going beyond the molecular cluster approximation and investigating dissolved Zn complexed by ligands such as Cl and CO_3 are now needed. From the experimental side, isotopic fractionation studies in which Zn speciation is controlled and the effect of parameters such as pH, Zn and ligand concentrations are investigated, are much required in order to validate the theoretical predictions. The complete understanding of equilibrium Zn isotope fractionation in relatively simple well-constrained experimental systems would help interpreting measurements done on natural samples and would allow more complex systems to be modelled.

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