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Toshiyuki Fujii, Frédéric Moynier, Marie-Laure Pons, Francis Albarède. The origin of Zn isotope fractionation in sulfides. *Geochimica et Cosmochimica Acta*, 2011, 75 (23), pp.7632-7643. 10.1016/j.gca.2011.09.036 . insu-00674540

HAL Id: insu-00674540

<https://insu.hal.science/insu-00674540>

Submitted on 4 Mar 2021

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Title	The origin of Zn isotope fractionation in sulfides
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Citation	Geochimica et Cosmochimica Acta (2011), 75(23): 7632-7643
Issue Date	2011-12
URL	http://hdl.handle.net/2433/151755
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Type	Journal Article
Textversion	author

Original Paper

The origin of Zn Isotope Fractionation in Sulfides

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Abstract:

Isotope fractionation of Zn between aqueous sulfide, chloride, and carbonate species (Zn^{2+} , $\text{Zn}(\text{HS})_2$, $\text{Zn}(\text{HS})_3^-$, $\text{Zn}(\text{HS})_4^{2-}$, $\text{ZnS}(\text{HS})^-$, ZnCl^+ , ZnCl_2 , ZnHCO_3^+ , and ZnCO_3) was investigated using *ab initio* methods. Only little fractionation is found between the sulfide species, whereas carbonates are up to 1‰ heavier than the parent solution. At pH>3 and under atmospheric-like CO_2 pressures, isotope fractionation of Zn sulfides precipitated from sulfidic solutions is affected by aqueous sulfide species and the $\delta^{66}\text{Zn}$ of sulfides reflect these in the parent solutions. Under high P_{CO_2} conditions, carbonate species become abundant. In high P_{CO_2} conditions of hydrothermal solutions, Zn precipitated as sulfides is isotopically nearly unfractionated with respect to a low-pH parent fluid. In contrast, negative $\delta^{66}\text{Zn}$ down to at least -0.6‰ can be expected in sulfides precipitated from solutions with pH>9. Zinc isotopes in sulfides and rocks therefore represent a potential indicator of mid to high pH in ancient hydrothermal fluids.

Keywords: Zinc, ligand, ocean, quantum chemical calculation, isotope fractionation

1. INTRODUCTION

Measurements of isotopic variations of Zn with a precision routinely better than 50 ppm have been reported in natural samples (see Albarede, 2004; Cloquet, 2008 for reviews). Presently, the interpretation of these isotopic variations is limited by our knowledge of the fractionation involved during chemical reactions, especially for species relevant to the present and ancient oceans, such as Zn chloride and Zn sulfides. Isotope fractionations created in Zn(II)-Zn(II) ligand exchange reactions (Maréchal and Albarède, 2002; Fujii et al., 2010) and in Zn(II)-Zn⁰ redox reactions (Kavner et al., 2008; Fujii et al., 2009a) have been experimentally observed. Preliminary estimates of Zn isotope fractionation were provided in abstract form by Schauble (2003), while extensive calculations using *ab initio* techniques allowed Zn isotope fractionation to be assessed for aquo-, chloro-, sulfato-, and other dissolved Zn²⁺ species (Black et al., 2011).

The role of sulfides is central to a broad range of prevalent geological scenarios and in particular the status of sulfur in ancient oceans is an outstanding issue (Canfield, 1998). Thermodynamic calculations for Zn sulfides and hydrosulfides have been carried out with the aim of assessing the chemistry of Proterozoic and Archean oceans (Saito et al., 2003). Hydrothermal vent solutions discharging either at mid-ocean ridges (Edmond et al., 1979) or along subduction zones (Mottl et al., 2004) comprise another environment dominated by sulfides. The solubility of sphalerite (ZnS) and speciation in sulfide solutions have also been studied (Bourcier and Barnes, 1987; Hayashi et al., 1990; Daskalakis and Helz, 1993; Tagirov et al., 2007; Tagirov and Seward, 2010). Tagirov et al. (2007) determined the stoichiometry and stability of Zn sulfide/hydrosulfide complexes at 373 K and concluded that the major species are

$\text{Zn}(\text{HS})_2^0$, $\text{Zn}(\text{HS})_3^-$, and $\text{ZnS}(\text{HS})^-$. Their Zn speciation model was consistent with that of Bourcier and Barnes (1987), but different from other models (Hayashi et al., 1990; Daskalakis and Helz, 1993), and was further expanded and strengthened in recent work (Tagirov and Seward, 2010). The present work takes on the task of evaluating Zn speciation and isotope fractionation among the different Zn sulfide species present in geological fluids between 298 and 573 K. It largely relies on the stability analysis of Tagirov et al. (2010) and complements the recent work by Black et al. (2011) on Zn isotope fractionation in solution.

2. COMPUTATIONAL METHODS

Orbital geometries and vibrational frequencies of aqueous Zn(II) species were computed using density functional theory (DFT) as implemented by the Gaussian03 code (Frisch et al., 2003). The DFT method employed here is a hybrid density functional consisting of Becke's three-parameter non-local hybrid exchange potential (B3) (Becke, 1993) with Lee-Yang and Parr (LYP) (Lee et al., 1988) non-local functionals. In a quantum chemical study, the convergence of the reaction energies of Zn(II) species is excellent in 6-311+G(d,p) or higher basis sets (Rulišek and Havlas, 1999). Hence, the 6-311+G(d,p) basis set, which is an all-electron basis set, was chosen for H, C, O, S, and Zn. For the solvation effect, the CPCM continuum solvation method (CPCM: conductor-like polarizable continuum model) was used. The geometry optimization and intramolecular vibrational frequency analysis were performed for the hydrated Zn ion, hydrated Zn carbonates, and hydrated Zn sulfides. For hydrated Zn chlorides, the results were reproduced from our previous study (Fujii et al., 2010).

3. RESULTS AND DISCUSSION

3.1 Basis for the isotope fractionation theory in systems at equilibrium

A chemical exchange reaction can be represented as two half-reactions,



or



where A and A' are the heavy and light isotopes of the element A, and X and Y represent ligands. The difference between half-reactions 1 and 2 corresponds to an isotopic exchange reaction between AX and AY,



The isotope separation factor α between AX and AY is defined as

$$\alpha = \frac{([A]/[A'])_Y}{([A]/[A'])_X} \quad (4)$$

where $([A]/[A'])_X$ and $([A]/[A'])_Y$ are the isotopic ratios of A/A' measured in the complexes AX (and A'X) and AY (and A'Y), respectively. The isotope enrichment factor is defined as $\alpha_m - 1$. Since α is close to 1, $\alpha - 1$ can be approximated as $\ln \alpha$.

Isotopic deviations in parts per 1000 are conventionally defined as

$$\delta = \left(\frac{([A]/[A'])_{\text{species}}}{([A]/[A'])_{\text{reference}}} - 1 \right) \times 1000 \quad (5)$$

If AX (and A'X) is the major component in the system, $\Sigma[A]/\Sigma[A']$ is approximated to be $([A]/[A'])_X$ such that an approximation expression $\delta \approx 10^3 \ln \alpha$ works.

The standard theory of chemical isotope fractionation is based on mass-dependent isotopic differences in vibrational energies of isotopologues (Urey, 1947; Bigeleisen and Mayer, 1947). The isotope enrichment factor is proportional to $\left(\frac{1}{m'} - \frac{1}{m} \right)$ with m and m' the masses of two isotopes (prime represents the light isotope). In a previous study on Zn isotope fractionation, we showed that the contribution of other effects, such as the nuclear field shift effect (Bigeleisen, 1996; Nomura et al., 1996; Fujii et al., 2009b) to $\ln \alpha$ is <10% (Fujii et al., 2010). Therefore, an adequate approximation of fractionation factors between different species may be obtained by the conventional mass-dependent theory (Bigeleisen and Mayer, 1947). All the calculations were made for the $^{66}\text{Zn}/^{64}\text{Zn}$ ratio which avoids odd even staggering (King, 1984; Aufmuth et al., 1987; Fricke and Heilig, 2004; Fujii et al., 2009b).

The isotope enrichment ($\ln \alpha$) due to the intramolecular vibrations can be evaluated from the reduced partition function ratio (RPFR) $(s/s')f$ (Bigeleisen and Mayer, 1947; Urey, 1947) defined as

$$\ln (s/s')f = \Sigma [\ln b(u_i') - \ln b(u_i)] \quad (6)$$

where

$$\ln b(u_i) = -\ln u_i + u_i/2 + \ln (1 - e^{-u_i}) \quad (7)$$

In this equation, ν stands for vibrational frequency, s for the symmetry number of the molecule, and $u_i = h\nu_i/kT$. The subscript i stands for the i th molecular vibrational level with primed variables referring to the light isotopologue. The isotope enrichment factor due to the molecular vibration can be evaluated from the frequencies summed over all the different modes. The partition function ratio $(s/s')^f$ for isotopologues A'X and AX (A'Y and AY, respectively) is noted β_X (β_Y , respectively). In the isotopic exchange reaction 3, isotope fractionation can be estimated from the relation $\ln \alpha \approx \ln \beta_Y - \ln \beta_X$.

In the present study, the optimized structures of hydrated Zn^{2+} and hydrated Zn sulfides were first analyzed for ^{64}Zn . For each complex, intramolecular vibrational frequencies (ν_i) were analyzed. By substituting ν_i into Eq. (7), $\ln b(u_i')$ was determined. Using the same molecular structures, ^{64}Zn was replaced by ^{66}Zn and the vibrational frequency analysis was performed again to obtain $\ln b(u_i)$, from which $\ln \beta$ was then determined.

3.2. Assessment of *ab initio* calculations

The isotope fractionation between hydrated Zn^{2+} and aqueous Zn chlorides has been investigated experimentally and theoretically at 294 K (Fujii et al., 2010). Calculations carried out for $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, $\text{Zn}(\text{H}_2\text{O})_{18}^{2+}$, $\text{ZnCl}(\text{H}_2\text{O})_5^+$, $\text{ZnCl}_2(\text{H}_2\text{O})_4$, $\text{ZnCl}_3(\text{H}_2\text{O})_3^-$, $\text{ZnCl}_3(\text{H}_2\text{O})^-$, $\text{ZnCl}_4(\text{H}_2\text{O})_2^{2-}$, and ZnCl_4^{2-} , allow for a comparison with the work of Black et al. (2011). As intramolecular vibrational modes and their frequencies depend on the cluster model and interatomic distances, the stability of each compound must first be demonstrated. We first tested the effect of solvation of Zn^{2+} ions by comparing

the small cluster $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, including only the first hydration shell (Fig. 1a and electronic annex, Fig. S1) with the large cluster $\text{Zn}(\text{H}_2\text{O})_{18}^{2+}$, in which the small cluster is surrounded by 12 H_2O molecules in a second hydration shell (see figure 1b of Li et al., 1996). In the present study, the CPCM continuum solvation method was tested. For $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, we used the dielectric constant of water $\epsilon = 78.3553$. The results are shown in Table 1 and were found to be consistent with those of Fig. 9 in Black et al. (2011) (see electronic annex, Tables S1, S2, and S3). The presence of the second hydration shell shortens the Zn-O bond distance by 0.014 Å in the first coordination shell. Applying the CPCM method further shortens this distance by 0.012 Å. The CPCM solvation method provides bond distances satisfactorily close to those obtained experimentally (Dreier and Rabe, 1986; Matsubara and Waseda, 1989; Maeda et al., 1995).

The calculated ν_1 frequencies (totally symmetric vibration, see Fig. S1) of $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ in this study and Fujii et al. (2010) are much smaller than the literature values obtained experimentally (Table 1). With the second hydration shell present, the calculated ν_1 frequency of $\text{Zn}(\text{H}_2\text{O})_{18}^{2+}$ agrees with the experimental value of 380 cm^{-1} (Yamaguchi et al., 1989). This frequency was not reproduced very well when the CPCM method was applied to a model including only the inner hydration shell.

Since the conventional Bigeleisen-Mayer equation (Bigeleisen and Mayer, 1947) involves vibrational frequencies, an accurate evaluation of ν_1 is in order. Besides ν_1 , other vibrational modes, *e.g.*, asymmetric modes of ν_3 and so on (see Fig. S1), are also important to evaluate RPFR (see Eqs. 6 and 7 and Black et al., 2011). The ν_2 and ν_3 frequencies are shown in Table 1. As for ν_1 , adding the second hydration shell increases the ν_2 and ν_3 frequencies and brings them closer to experimental observations (Rudolph

and Pye, 1999; Mink et al., 2003). Addition of the second hydration shell is therefore more effective than resorting to the CPCM solvation method.

The $\ln \beta$ values at 273, 423, and 573K (25, 150, and 300°C, respectively) calculated by using Eqs. (6) and (7) are shown in Table 2. The accuracy in RPFRs estimated by *ab initio* method is discussed in Rustad et al. (2010). It is clear that applying the CPCM solvation method does not significantly affect the value of $\ln \beta$, whereas adding a second hydration shell with 12 H₂O molecules increases $\ln \beta$ by 0.3‰ at 298 K. A similar phenomenon was found in our previous study on Pd²⁺ isotope fractionation (Fujii et al., in press).

3.3. β -factors of aqueous Zn sulfides

The structure of the Zn sulfides was calculated with small cluster models without additional shells. Zn²⁺ and Zn hydrogensulfides are related through the following stepwise reactions,





190

191 *Calculations for ZnSH⁺.*

192 The formation of Zn mono-hydrogensulfide has been suggested on the basis of
 193 voltammetric data (Zhang and Millero, 1994), but was later questioned (Luther et al.,
 194 1996). Reaction 8 was disregarded by studies on sphalerite (ZnS) solubility in sulfide
 195 solutions (Bourcier and Barnes, 1987; Hayashi et al., 1990; Daskalakis and Helz, 1993;
 196 Tagirov et al., 2007; Tagirov and Seward, 2010). Though we tested the structural
 197 optimization of ZnHS(H₂O)₅⁺, this model complex is unstable and deforms into
 198 ZnHS(H₂O)₄⁺ with the 5th water molecule moving out of the inner coordination shell,
 199 which suggests that the stability constant of reaction 8 is very small. A
 200 hydroxide-hydrogensulfide species, Zn(OH)HS⁺, has been reported (Bourcier and
 201 Barnes, 1987; Hayashi et al., 1990), but its existence was not confirmed (Tagirov et al.,
 202 2007; Tagirov and Seward, 2010).

203

204 *Calculations for Zn(HS)₂.*

205 In a theoretical study on Zn sulfides (Tossell and Vaughan, 1993), a tetrahedral
 206 structure Zn(HS)₂(H₂O)₂ has been reported as Zn(HS)₂. The structure of
 207 bis-hydrogensulfide for six-coordination transition metals is considered to be similar to
 208 that of *trans*-Mn(HS)₂(H₂O)₄ (Rickard and Luther, 2006). We calculated the optimized
 209 structure for the recommended structure Zn(HS)₂(H₂O)₄ (Fig. 1b) and the bond lengths
 210 are shown in Table 1. The ln β value at 298 K is 2.72%.

211

212 *Calculations for $\text{Zn}(\text{HS})_3^-$.*

213 The calculations for the 6-coordinated $\text{Zn}(\text{HS})_3(\text{H}_2\text{O})_3^-$ did not converge. HS^- forms
214 stronger bonds with Zn^{2+} than H_2O , and 3 HS^- molecules tend to form a triangle, with
215 Zn^{2+} at the center (see figure 1 of Tossell and Vaughan, 1993). Tossell and Vaughan
216 (1993) reported that $\text{Zn}(\text{HS})_3^-$ and $\text{Zn}(\text{HS})_3(\text{OH})^{2-}$ are the most stable of the
217 tri-hydrogensulfide species. The hydrolyzed species $\text{Zn}(\text{HS})_3(\text{OH})^{2-}$ has been
218 considered in earlier solubility studies of sphalerites (Hayashi et al., 1990; Daskalakis et
219 al., 1993), but its existence was later dismissed (Tagirov et al., 2007; Tagirov and
220 Seward, 2010).

221 The existence of a species $\text{Zn}(\text{HS})_3^-$ lacking direct Zn-water coordination is
222 unlikely in aqueous solution. Tossell and Vaughan (1993) reported the presence of the
223 mono-hydrated tri-hydrogensulfide species, $\text{Zn}(\text{HS})_3\text{H}_2\text{O}^-$, and our calculations
224 reproduced this structure (see figure 1 of Tossell and Vaughan, 1993). $\text{Zn}(\text{HS})_3$ keeps
225 the triangular plane with one H_2O molecule bound to the plane via a hydration bond
226 ($\text{H}_2\text{O}-\text{Zn}^{2+}$) and $\text{OH}_2\text{-SH}$ hydrogen bonds. The hydrogen bond appears stronger than the
227 hydration bond, which suggests that an extra H_2O molecule may bind to the opposite
228 side of the $\text{Zn}(\text{HS})_3$ plane to form $\text{Zn}(\text{HS})_3(\text{H}_2\text{O})_2^-$. The structure after convergence is
229 shown in Fig. 1c. However, even though the plane symmetric arrangement with two
230 H_2O molecules with respect to the $\text{Zn}(\text{HS})_3$ plane is possible, the Gibbs free energy was
231 1.09 kJ/mol larger and this model complex is therefore not chosen.

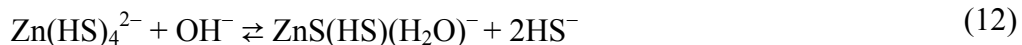
232 The bond distances are shown in Table 3. The longer Zn-O bond distance
233 suggests that the H_2O molecules possibly are bound to $\text{Zn}(\text{HS})_3$ via the hydrogen bonds
234 of $\text{OH}_2\text{-SH}$. The $\ln \beta$ value at 298 K is 3.03‰ (Table 2).

Calculations for $\text{Zn}(\text{HS})_4^{2-}$.

Solubility measurements of sphalerites in sulfide solutions (Bourcier and Barnes, 1987; Hayashi et al., 1990; Daskalakis and Helz, 1993) considered the presence of a tetra-hydrogensulfide species $\text{Zn}(\text{HS})_4^{2-}$; its mole fraction is expected to decrease with temperature (Tagirov and Seward, 2010). A possible tetrahedral structure (Fig. 1d) was suggested by Tossell and Vaughan (1993). The tetrahedral structure of $\text{Zn}(\text{HS})_4^{2-}$ is similar to a unit cell of Zn sulfide clusters (Luther et al., 1999; Luther and Rickard, 2005). Our results are shown in Tables 2 and 3. The $\ln \beta$ value at 298 K shows the smallest value (2.19%, Table 2) of all Zn sulfides.

Calculations for $\text{ZnS}(\text{HS})^-$.

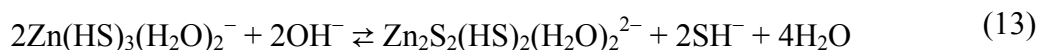
A distinctive feature in the solubility trend of sphalerite calculated by Tagirov et al. (2007) and Tagirov and Seward (2010) is that $\text{ZnS}(\text{HS})^-$ appears to be a prevalent sulfide species at $\text{pH} > 10$ and temperatures < 473 K. With increasing pH, complexation proceeds from $\text{Zn}(\text{HS})_3^-$ to $\text{Zn}(\text{HS})_4^{2-}$ and $\text{ZnS}(\text{HS})^-$ (Tagirov and Seward, 2010). Formation of $\text{ZnS}(\text{HS})^-$ from $\text{Zn}(\text{HS})_4^{2-}$ with increasing pH results from the reaction



A few *ab initio* calculation studies on anhydrous Zn sulfides (Cini, 1999) or clusters of Zn sulfides (Luther et al., 1999; Luther and Rickard, 2005) have been reported. To the best of our knowledge, structural data of monomeric $\text{ZnS}(\text{HS})^-$ in aqueous solutions are

not available. Spatially, water molecules may interact with Zn(II) in ZnS(HS)^- as $\text{ZnS(HS)(H}_2\text{O)}_n^-$. The coordination number of Zn(II) in the monomeric species $\text{ZnS(HS)(H}_2\text{O)}^-$ is three, but this coordination number is too small if this species exists in aqueous solution. Since the aggregation of complexes increases the coordination probability, $\text{ZnS(HS)(H}_2\text{O)}^-$ is considered to be a simplified formula of polymerized species $n[\text{ZnS(HS)(H}_2\text{O)}^-]$. Let us consider a dimer for $n = 2$.

Stereochemically, dimerization of ZnS(HS)^- from $\text{Zn(HS)}_3(\text{H}_2\text{O)}_3^-$ may be natural (see Fig. 1c and 1e).



where $\text{Zn}_2\text{S}_2(\text{HS})_2(\text{H}_2\text{O)}_2^{2-}$ can be expressed as $2[\text{ZnS(HS)(H}_2\text{O)}^-]$. Zn(II) has a coordination number of 5 in this species. Since S^{2-} has the tetrahedral coordination property, two S^{2-} ions bridging to two Zn^{2+} ions may also bind to H_2O in the outer sphere. More H_2O molecules may be arranged on the triangular Zn(HS)_3 plane. $\text{ZnS(HS)(H}_2\text{O)}_n^-$ with $n \geq 2$ may exist.

Zn(HS)_3^- and ZnS(HS)^- possess the trigonal planar of ZnS_3 core, while Zn(HS)_4^{2-} is tetrahedral. Large entropic changes via structural changes in the reaction $\text{Zn(HS)}_3^- \leftrightarrow \text{Zn(HS)}_4^{2-} \leftrightarrow \text{ZnS(HS)}^-$ are expected due to the existence of intermediate state Zn(HS)_4^{2-} . With the increase of temperature, the mole fraction of Zn(HS)_4^{2-} drastically decreases (Tagirov and Seward, 2010). This suggests a direct reaction pathway between Zn(HS)_3^- and ZnS(HS)^- at high temperatures. This reaction path of

reaction 13 would be entropically favorable. The bond distances of $2[\text{ZnS}(\text{HS})\text{H}_2\text{O}^-]$ are shown in Table 3. The $\ln \beta$ value at 298 K is 2.63‰ (Table 2).

Calculations for Zn carbonates.

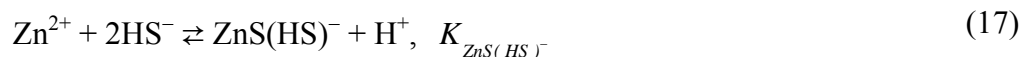
In the present work, we calculated the $\ln \beta$ values for Zn isotope fractionation (Table 2) for hydrated Zn carbonates, $\text{ZnHCO}_3(\text{H}_2\text{O})_4$, and $\text{ZnCO}_3(\text{H}_2\text{O})_4$, in which HCO_3^- and CO_3^{2-} are treated as bidentate ligands (see Figs. 1f and 1g) using the same techniques as Fujii et al. (2011) for Ni. Zinc is isotopically heavy in carbonates relative to hydrated Zn^{2+} and Zn sulfide species. The $\ln \beta$ values are larger than those of $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, Zn sulfides, and Zn chlorides. They compare with the $\ln \beta$ values reported by Black et al. (2011) on Zn sulfates. Upon reduction of sulfates to sulfides in the presence of carbonate ions, a strong fractionation of Zn isotopes may be expected in the sulfide-carbonate system.

3.4. Zn isotope systematics between aqueous sulfides and chlorides

Isotope fractionation relevant to $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, $\text{Zn}(\text{HS})_2(\text{H}_2\text{O})_4$, $\text{Zn}(\text{HS})_3(\text{H}_2\text{O})_2^-$, $\text{Zn}(\text{HS})_4^{2-}$, $2[\text{ZnS}(\text{HS})\text{H}_2\text{O}^-]$, $\text{ZnCl}(\text{H}_2\text{O})_5^+$, $\text{ZnCl}_2(\text{H}_2\text{O})_4$, $\text{ZnHCO}_3(\text{H}_2\text{O})_4^+$, and $\text{ZnCO}_3(\text{H}_2\text{O})_4$ will now be evaluated. The structure and $\ln \beta$ of Zn chlorides were reproduced from our previous study (Fujii et al., 2010) with calculations extended to higher temperatures. The temperature dependence of $\ln \beta$ can be estimated from the values compiled in Table 2. The total range of variation of $\ln \beta$ at 298 K is ~2‰. We calculated the speciation and isotopic fractionation of Zn for a total concentration of sulfur $\Sigma[\text{S}]$ of 0.1 M in the absence of Cl^- ($[\text{Cl}^-] = 0$ M) and carbonates ($\Sigma[\text{C}] = 0$ M) at

298, 423, and 573 K as a function of pH. In our calculation, free Cl^- concentration is just treated as a parameter without considering association/dissociation reactions of HCl and chlorides at various temperatures. In principle, activities should be used throughout rather than concentrations, but the precise compositions of hydrothermal solutions are rarely known, and uncertainties on isotope fractionation attached to the non-ideal character of electrolyte solutions are certainly negligible with respect to those resulting from the poorly constrained chemistry of hydrothermal systems. As a result, the activity coefficients were considered equal to unity. As a dilute system, molar concentrations are used instead of molal concentrations. All calculations were performed under an assumption that the molecular structures remain the same by increasing temperature.

The following chemical equilibrium reactions were investigated,



It should be noted that, in the present study, we use K for cumulative formation constant β in order to avoid confusion about $\ln \beta$ of isotope fractionation.

Under reducing conditions with negligible sulfate formation, the total concentration of sulfur ($\Sigma[S] = 0.1 \text{ M}$) is controlled by the following dissociation reaction,

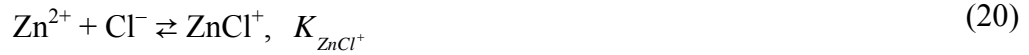


where we used the relation,

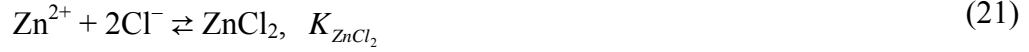
$$\log \frac{[\text{HS}^-]}{[\text{H}_2\text{S}]} = -\text{p}K_a + \text{pH} \quad (19)$$

The stability constants and acid dissociation constants ($\text{p}K_a$) at 298, 423, and 573 K used are listed in Table 4. Since $\text{p}K_a$ was determined under the existence of Na^+ , strictly, it includes an effect of NaHS dissociation.

We also calculated the speciation and isotopic fractionation of Zn isotologues under typical hydrothermal conditions, with $\Sigma[S] = 5 \text{ mM}$ (Von Damm, 1990) and $[\text{Cl}^-] = 0.55 \text{ M}$ (Macleod et al., 1994) at 298, 423, and 573 K and for variable pH. We set P_{CO_2} at 50 bar ($\log P_{\text{CO}_2} = 1.6$), which corresponds to a water (total) pressure of 10^5 Pa (1 kbar) and a mole fraction of CO_2 of 5 percent (Rose et al., 1996). Such values conveniently describe the conditions at about 3 km below the sea floor. The following chemical equilibrium reactions also were investigated,



336



337



338



339

340 For carbonates, the following gas-liquid equilibrium reactions were considered.

341



342



343

344 The ionization of carbonic acid at elevated temperatures has been studied by Read

345 (1975) and Patterson et al. (1982, 1984). The acid dissociation constant between the

346 hydrogen carbonate ion (HCO_3^-) and the carbonate ion (CO_3^{2-}) is the ratio of $K_{\text{HCO}_3^-}$

347 and $K_{\text{CO}_3^{2-}}$. These values at 298, 423, and 573 K (Smith et al., 1986), in which the

348 original data are taken from (Patterson et al., 1982; 1984), are shown in Table 4.

Because of the broad relevance of carbon dioxide to geological environments, we first investigated the effect of P_{CO_2} on Zn isotope variability of Zn in sulfidic hydrothermal environments. As a reference, speciation and isotope fractionation are first investigated for hydrothermal solutions placed under the low P_{CO_2} typical of equilibration with the modern atmosphere. Then, the discussion is extended to conditions of high P_{CO_2} in order to constrain Zn isotope fractionation in solutions equilibrated with a high- P_{CO_2} atmosphere or circulating in deep-seated hydrothermal systems.

The results are shown in Figs. 3, 4, and 5. Figs 3a, 4a, and 5a show quite good agreement with the reported mole fractions of aqueous Zn sulfide species estimated from stability constants of reactions 14-17 and solubility products of ZnS(crystal) (Tagirov and Seward, 2010). In the present study, $K_{ZnHCO_3^+}$ and K_{ZnCO_3} at the standard temperature 298 K (Zirino and Yamamoto, 1972) were used for 423 and 573 K due to lack of reliable data of aqueous Zn carbonates at high temperature. Even if a tenfold larger $K_{ZnHCO_3^+}$ were used for 573 K (Fig 5b), the mole fraction of $ZnHCO_3^+$ would not visibly increase. Variations of K_{ZnCO_3} mainly changes the mole fractions of $ZnCO_3$ and $ZnS(HS)^-$ but have little effect on the concentrations of other species. Increasing log K_{ZnCO_3} by one unit increases the mole fraction of $ZnCO_3$ and decreases that of $ZnS(HS)^-$ by ~25% (see electronic annex, Fig. S2).

Isotope fractionation of Zn observed as $\delta^{66}Zn$ was estimated as shown in Figs. 3c, 3d, 4c, 4d, 5c, and 5d. The $\delta^{66}Zn$ value was calculated as follows. The bulk $^{66}Zn/^{64}Zn$ ratio is

$$\frac{\Sigma[^{66}\text{Zn}]}{\Sigma[^{64}\text{Zn}]} = \frac{[^{66}\text{Zn}^{2+}] + [^{66}\text{Zn}(\text{HS})_2] + [^{66}\text{Zn}(\text{HS})_3^-] + [^{66}\text{Zn}(\text{HS})_4^{2-}] + [^{66}\text{ZnS}(\text{HS})^-] + [^{66}\text{ZnCl}^+] + [^{66}\text{ZnCl}_2] + [^{66}\text{ZnHCO}_3^+] + [^{66}\text{ZnCO}_3]}{[^{64}\text{Zn}^{2+}] + [^{64}\text{Zn}(\text{HS})_2] + [^{64}\text{Zn}(\text{HS})_3^-] + [^{64}\text{Zn}(\text{HS})_4^{2-}] + [^{64}\text{ZnS}(\text{HS})^-] + [^{64}\text{ZnCl}^+] + [^{64}\text{ZnCl}_2] + [^{64}\text{ZnHCO}_3^+] + [^{64}\text{ZnCO}_3]} \quad (26)$$

Stability constants were calculated from $\ln \beta$ values. For example,

$$\ln \frac{K_{\text{Zn}(\text{HS})_2}(^{66}\text{Zn})}{K_{\text{Zn}(\text{HS})_2}(^{64}\text{Zn})} = \ln \frac{[^{66}\text{Zn}(\text{HS})_2]/[^{64}\text{Zn}(\text{HS})_2]}{[^{66}\text{Zn}^{2+}]/[^{64}\text{Zn}^{2+}]} \\ = \ln \beta_{\text{Zn}(\text{HS})_2} - \ln \beta_{\text{Zn}^{2+}} \quad (27)$$

The value $\Sigma[\text{Zn}] = 10^{-6.1}$ M (Tagirov and Seward, 2010) was used, but is inconsequential for the speciation calculation. The effect of ionic strength was neglected and activity coefficients of all species were set to be unity in a diluted system, which would be of no practical importance for isotope ratios.

3.5 Zn isotope variability in solutions at low to intermediate temperatures

Low P_{CO_2} conditions.

Isotope fractionation between natural fluids and precipitates occurs when Zn distributes itself between sphalerite, the prevalent Zn ore, and the parent fluid. Figures 3-5 indicate that, as expected from the order of $\ln \beta$ (Figure 2), the various aqueous Zn sulfide complexes are all isotopically lighter than Zn^{2+} and Zn chlorides. Zinc isotope fractionation in sulfide-rich solutions is controlled by the respective mole fractions of hydrated Zn^{2+} and aqueous sulfides and therefore is predicted to be pH-dependent. At

pH<3, Zn is largely present as Zn^{2+} in fresh water and as Zn chlorides at seawater chlorinities. High chlorine contents change the charge balance and therefore shift the dependence of speciation with pH, but, overall, affect isotope fractionation patterns only slightly (see electronic, Figs. S3, S4, and S5). Under conditions typical of equilibration with the atmosphere, carbonate complexes can safely be neglected (Zirino and Yamamoto, 1972). Sulfides precipitating from hydrothermal solutions should be isotopically lighter than the solution, but the extent of isotope fractionation decreases with temperature. Zn isotope fractionation between the plausible precursor species of sphalerite, $\text{Zn}(\text{HS})_2$ at low pH and $\text{Zn}(\text{HS})_4^{2-}$ and/or $\text{ZnS}(\text{HS})^-$ at high pH, is very small. At pH>3, the dominant Zn species are aqueous sulfides (Tagirov and Seward, 2010). Under the assumption that the isotopic composition of sphalerite is inherited from the precursor species, little isotope fractionation between sphalerite and the fluid is therefore expected (< 0.25‰) at 423 K and even less at higher temperatures.

In sulfide-free oxic seawater and fresh water equilibrated with the atmosphere, metallic ion, chloride, hydroxide, and carbonate complexes dominate zinc speciation, while Zn sulfate is a minor species (Zirino and Yamamoto, 1972; Turner et al., 1981; Stanley and Byrne, 1990; Black et al., 2011). Zn in marine carbonates is about 1‰ heavier (Pichat et al., 2003) than seawater ($\delta^{66}\text{Zn}\sim 0\text{‰}$) (Bermin et al., 2006), which is consistent with Zn isotope fractionation observed at ~298 K between aqueous carbonate species and the metallic ion or its chloride (see electronic annex, Fig. S6). Zn-O bonds, as in zincite (ZnO) (Schauble et al. 2003), zinc sulfates (Black et al., 2011), and presumably other oxo-anions tend to concentrate heavy Zn. An enrichment of Zn heavy isotopes is therefore expected for zinc carbonates. Here we further assume that Zn

isotope fractionation between solid carbonates and the dissolved species ZnCO_3 can be neglected.

High P_{CO_2} conditions.

Carbonate, which is usually a minor species in surface waters, becomes a major player in hydrothermal solutions when P_{CO_2} rises at depth. Figs. 3b, 3d, 4b, 4d, 5b, and 5d show that the presence of carbonate ions brings about a stark contrast between regions of low pH (<8) and high pH (>9). We will restrict the discussion to sphalerite precipitation when smithsonite (ZnCO_3) does not reach saturation. At low pH (pH < $\text{p}K_{\text{HCO}_3^-}$), the abundance of the aqueous ZnCO_3 species is very low and sphalerite precipitates with nearly the same $\delta^{66}\text{Zn}$ as the original fluid, *i.e.*, with very little fractionation. In contrast, at pH>9, most Zn is in aqueous carbonate form. ZnS is considered to be formed from major sulfides $\text{ZnS}(\text{HS})^-$ and/or $\text{Zn}(\text{HS})_4^{2-}$ via polymerization and dehydration. If isotope fractionation upon precipitation can be neglected, the values of $\delta^{66}\text{Zn}$ for $\text{ZnS}(\text{HS})^-$ and $\text{Zn}(\text{HS})_4^{2-}$ are representative of those eventually found in ZnS . Sphalerite is therefore expected to possess negative $\delta^{66}\text{Zn}$ values. Zinc is isotopically more negative in sphalerite with respect to the fluid, by ~1.5‰ at 298 K, ~0.8‰ at 423 K, and ~0.4‰ at 573 K (see $\delta^{66}\text{Zn}$ of $\text{ZnS}(\text{HS})^-$ and/or $\text{Zn}(\text{HS})_4^{2-}$ at pH >9). Strongly negative $\delta^{66}\text{Zn}$ in sphalerite therefore represents a potential indicator of high pH in low- to high-temperature hydrothermal fluids.

The narrow range of Zn isotope fractionation, mostly 0.0 to 0.6‰ in natural sphalerite from continental environments (Albarede, 2004; Kelley et al., 2009) and in most serpentines (Pons et al., 2010), together with the lack of strong isotope

fractionation between ZnS and hydrothermal vent fluid from mid-ocean ridges at temperatures >523 K (John et al., 2008) can be explained by the predominance of chloride complexes and aquated Zn^{2+} ion in solutions at $\text{pH} < 7$. These observations concur with limited computational evidence that sphalerite is not fractionated with respect to tetrahedral $[\text{ZnCl}_4]^{2-}$ (Schauble et al., 2003). Sphalerite precipitation therefore seems to take place by disproportionation of an aqueous sulfide species, most likely $\text{Zn}(\text{HS})_2(\text{H}_2\text{O})_4$ and $\text{ZnS}(\text{HS})\text{H}_2\text{O}^-$. Occasionally high $\delta^{66}\text{Zn}$ in hydrothermal fluids (John et al., 2008) may reflect the prevalence of Zn leached out of carbonate and FeMn-hydroxides ($\delta^{66}\text{Zn} > 0.6$ ‰) (Maréchal et al., 2000; Pichat et al., 2003) and not from a basaltic source ($\delta^{66}\text{Zn} \sim 0.3$ ‰).

In contrast, the negative $\delta^{66}\text{Zn}$ observed by Pons et al. (2010) in the mud serpentine volcanoes of the Mariana associated with high-pH (10-12) interstitial fluids (down to -0.2 ‰) (Mottl et al. 2004; Hulme et al., 2010), and by Mason et al. (2005) in island arc-type base-metal deposits from the Urals (down to -0.4 ‰) carry the signature of fractionation by sulfides in island arc hydrothermal solutions dominated by sulfate and carbonates. Zinc-sulfate complexes are weak and much less abundant than chloride and hydroxide complexes, even with the rather high sulfate contents typical of seawater (Stanley and Byrne, 1990; Mottl et al. 2004; Black et al., 2011). The negative $\delta^{66}\text{Zn}$ values of sulfides precipitated from hydrothermal fluids therefore signal the stability of Zn carbonates and hence pH in excess of the second pK_a of carbonic acid. Zinc isotope compositions in sulfides and rocks are potentially helpful in distinguishing low-pH from high-pH hydrothermal solution.

CONCLUSIONS

Isotope fractionation of Zn in aqueous sulfidic solutions was found to be controlled by aqueous zinc sulfide species, and for high P_{CO_2} conditions, by zinc carbonate species. In solutions equilibrated with the atmosphere, Zn is isotopically unfractionated in sulfides and isotopically heavy in carbonates. Under the high P_{CO_2} conditions of hydrothermal solutions, Zn precipitated as sulfides is isotopically nearly unfractionated with respect to a low-pH parent fluid. Negative $\delta^{66}\text{Zn}$ down to 0.6‰ can be expected in sulfides precipitated from solutions with high P_{CO_2} and a pH > 9. Zn isotopes in sulfides and rocks therefore represent a potential indicator of mid to high pH in ancient hydrothermal fluids.

ACKNOWLEDGMENTS

The authors thank the anonymous reviewers for their useful suggestions, and are grateful to Associate Editor Edwin Schauble, for catching a major problem in an early version of this manuscript and for constructive comments on the manuscript. The authors thank Janne Blichert-Toft for help in improving the English.

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Table 1 Zn-O bond distances and ν_1 frequencies determined for hydrated Zn^{2+} .

Species	Method ^a	Zn-O (Å)	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)	Reference
$\text{Zn}(\text{H}_2\text{O})_6^{2+}$	DFT	2.128	333	-	-	Fujii et al. (2010)
$\text{Zn}(\text{H}_2\text{O})_6^{2+}$	DFT ^b	2.128	333	219	294	This study
$\text{Zn}(\text{H}_2\text{O})_6^{2+}$	DFT ^c	2.102	353	227	317	This study
$\text{Zn}(\text{H}_2\text{O})_{18}^{2+}$	DFT ^d	2.114	380	-	-	Fujii et al. (2010)
$\text{Zn}(\text{H}_2\text{O})_{18}^{2+}$	DFT ^d	2.114	380	298	362	This study
-	XRD	2.08	-	-	-	Tossel (1991)
-	XRD	2.15	-	-	-	Maeda et al. (1995)
-	AXN	2.10-2.15	-	-	-	Matsubara and Waseda (1989)
-	EXAFS	2.05-2.07	-	-	-	Dreier and Rabe (1986)
-	Raman	-	390±10	-	-	Irish et al. (1963)
-	Raman	-	379±5	-	-	Yamaguchi et al. (1989)
-	Raman	-	385	-	-	Maeda et al. (1995)
-	Raman, IR	-	390±2	270±5	365±5	Rudolph and Pye (1999)
-	Raman, IR	-	389	360	386	Mink et al. (2003)

^a DFT (density functional theory), XRD (x-ray diffraction), AXN (anomalous x-ray scattering), EXAFS (extended x-ray absorption fine structure), IR (infrared).

^b DFT calculation results with various basis sets are given in electronic annex, Tables S1 and S2.

^c CPCM continuum solvation method was applied.

^d 12 H_2O molecules were arranged around $\text{Zn}(\text{H}_2\text{O})_6^{2+}$.

Table 2 Logarithm of the reduced partition function, $\ln \beta$, for isotope pair $^{66}\text{Zn}/^{64}\text{Zn}$.

Species	$\ln \beta$ at 298K (‰)	$\ln \beta$ at 423K (‰)	$\ln \beta$ at 573K (‰)
$\text{Zn}(\text{H}_2\text{O})_6^{2+ a}$	3.263 3.280 ^b	1.659 1.660 ^b	0.915 0.913 ^b
$\text{Zn}(\text{H}_2\text{O})_{18}^{2+ a}$	3.576	1.819	1.004
$\text{Zn}(\text{HS})_2(\text{H}_2\text{O})_4$	2.717	1.384	0.764
$\text{Zn}(\text{HS})_3(\text{H}_2\text{O})_2^-$	3.028	1.535	0.845
$\text{Zn}(\text{HS})_4^{2-}$	2.190	1.101	0.604
$\text{ZnS}(\text{HS})\text{H}_2\text{O}^-$	2.628	1.326	0.728
$\text{ZnCl}(\text{H}_2\text{O})_5^{+ a}$	3.142	1.599	0.882
$\text{ZnCl}_2(\text{H}_2\text{O})_4^a$	2.956	1.495	0.822
$\text{ZnHCO}_3(\text{H}_2\text{O})_4^+$	3.439	1.754	0.969
$\text{ZnCO}_3(\text{H}_2\text{O})_4$	3.990	2.050	1.137

^a Calculated structures (Fujii et al., 2010) were reproduced.

^b Applying the CPCM continuum solvation method.

Table 3 Bond distances calculated for Zn sulfides.

Species	Bond ^a , Zn-O (Å)	Bond ^a , Zn-S (Å)
Zn(HS) ₂ (H ₂ O) ₄	2.434(2) 2.514(2)	2.295(2)
Zn(HS) ₃ (H ₂ O) ₂	3.536(2)	2.300(2) 2.324(1)
Zn(HS) ₄	–	2.450(4)
ZnS(HS)H ₂ O [–]	3.412(2) ^b	2.331(2) ^b 2.365(1)

^a Numbers of bonds are shown in parentheses.

^b Shared with another Zn²⁺.

Table 4 Stability constants of Zn sulfide and chloride systems.

	298K	423K	573K	Reference
$\log K_{Zn(HS)_2}$	9.40	9.82	12.56 ^a	Tagirov and Seward (2010)
$\log K_{Zn(HS)_3^-}$	13.06 ^a	12.39 ^b	14.41 ^a	Tagirov and Seward (2010)
$\log K_{Zn(HS)_4^{2-}}$	14.47	12.02 ^a	11.80 ^a	Tagirov and Seward (2010)
$\log K_{ZnS(HS)^-}$	3.41	2.69	2.47 ^a	Tagirov and Seward (2010)
$\log K_{ZnCl^+}$	-0.03 ^c	2.89	6.53 ^c	Ruaya and Seward (1986)
$\log K_{ZnCl_2}$	0.13 ^c	2.96	7.51 ^c	Ruaya and Seward (1986)
$\log K_{ZnHCO_3^+}$	2.1	2.1 ^d	2.1 ^d	Zirino and Yamamoto (1972)
$\log K_{ZnCO_3}$	5.3	5.3 ^d	5.3 ^d	Zirino and Yamamoto (1972)
$\log K_{HCO_3^-}$	-6.35	-6.74	-8.50	Smith et al. (1986)
$\log K_{CO_3^{2-}}$	-16.69	-16.98	-19.82	Smith et al. (1986)
pK _a	6.99	6.49	7.89	Suleimenov and Seward (1997)

^a Values are shown in Appendix C in Tagirov and Seward (2010).

^b Value for 373K was used. The value for 423K did not reproduce the speciation calculation of Tagirov and Seward (2010).

^c Calculated from equation 23 in Ruaya and Seward (1986).

^d Stability constants at 298 K.

Figure captions

Figure 1 Molecular structures of hydrated Zn^{2+} and aqueous Zn sulfides. Structures are drawn by using GaussView3.0 (Gaussian Inc.). a) $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, b) $\text{Zn}(\text{HS})_2(\text{H}_2\text{O})_4$, c) $\text{Zn}(\text{HS})_3(\text{H}_2\text{O})_2^-$, d) $\text{Zn}(\text{HS})_4^{2-}$, e) $\text{Zn}_2\text{S}_2(\text{HS})_2(\text{H}_2\text{O})_2^{2-} = 2[\text{ZnS}(\text{HS})(\text{H}_2\text{O})^-]$, f) $\text{ZnHCO}_3(\text{H}_2\text{O})_4^+$, and g) $\text{ZnCO}_3(\text{H}_2\text{O})_4$.

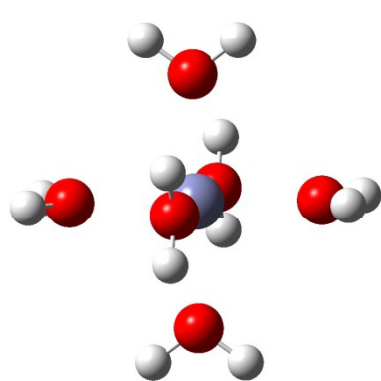
Figure 2 Temperature dependence of $\ln \beta$. The $\ln \beta$ values shown in Table 2 are fitted by linear functions of T^{-2} .

Figure 3 Mole fractions of Zn species and Zn isotopic variations as functions of pH at 298 K. a) Mole fractions of Zn species in Cl^- and carbonate free hydrous fluid under $\Sigma[\text{S}]=0.1$ M, b) Mole fractions of Zn species with $\Sigma[\text{S}]=5$ mM and $[\text{Cl}^-] = 0.55$ M under $P_{\text{CO}_2} = 50$ bar, c) Species $\delta^{66}\text{Zn}$ relative to the bulk solution in Cl^- and carbonate free hydrous fluid, and d) $\delta^{66}\text{Zn}$ under the hydrothermal condition of b). Dotted lines at 0‰ in c) and d) show $\delta^{66}\text{Zn}$ of bulk solution (averaged $\delta^{66}\text{Zn}$ in the whole solution). $\Sigma[\text{Zn}]$ was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).

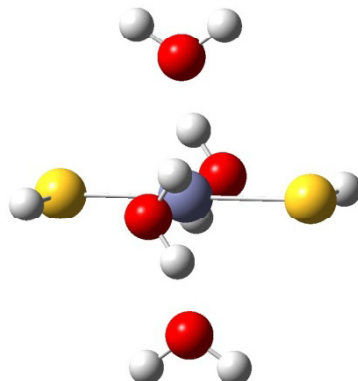
Figure 4 Mole fractions of Zn species and Zn isotopic variations as functions of pH at 423 K. Panels a-d : see caption of Fig. 3. Mole fraction of Zn^{2+} in Fig. 4b is 0.14% at pH=2 and smaller than that at pH>2. The maximum value of $\text{Zn}(\text{HS})_4^{2-}$ mole fraction is 0.06% at pH=7.1 (Fig. 4b). Dotted lines in c) and d) mean $\delta^{66}\text{Zn}$ of bulk solution (averaged $\delta^{66}\text{Zn}$ in the whole solution). $\Sigma[\text{Zn}]$ was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).

Figure 5 Mole fractions of Zn species and Zn isotopic variations as functions of pH at 573 K. Panels a-d : see caption of Fig. 3. Mole fraction of Zn^{2+} in Fig. 5b is smaller than 0.001%. The maximum value of $\text{Zn}(\text{HS})_4^{2-}$ mole fraction is 0.02% (Fig. 5a) or

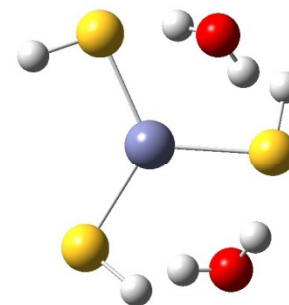
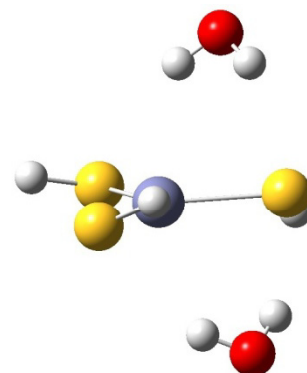
749 0.0002% (Fig. 5b) at pH=9.3. The maximum value of ZnHCO_3^+ mole fraction is 0.1%
750 at pH= 10.5 (Fig. 5b). Dotted lines in c) and d) mean $\delta^{66}\text{Zn}$ of bulk solution (averaged
751 $\delta^{66}\text{Zn}$ in the whole solution). $\Sigma[\text{Zn}]$ was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).
752
753
754
755



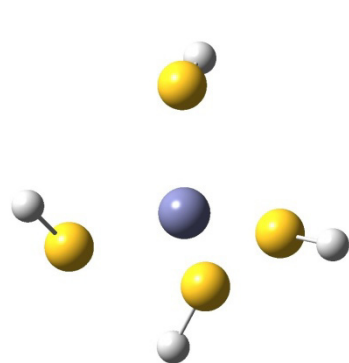
a) $\text{Zn}(\text{H}_2\text{O})_6^{2+}$



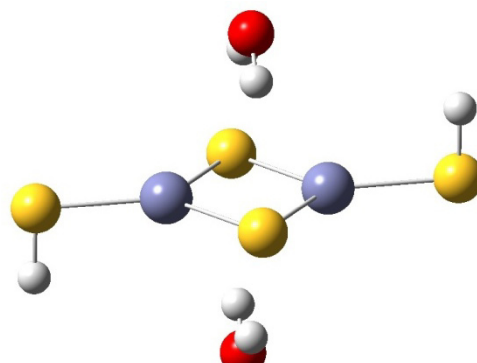
b) $\text{Zn}(\text{HS})_2(\text{H}_2\text{O})_4$



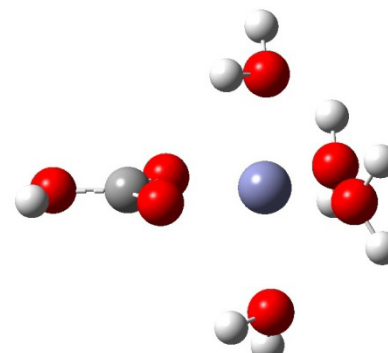
c) $\text{Zn}(\text{HS})_3(\text{H}_2\text{O})_2^-$: side view (left), top view (right)



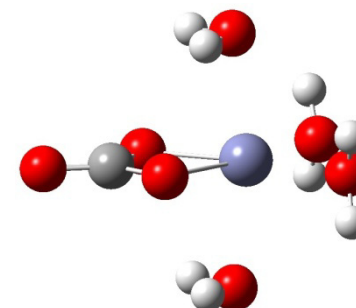
d) $\text{Zn}(\text{HS})_4^{2-}$



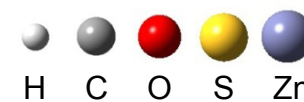
e) $\text{Zn}_2\text{S}_2(\text{HS})_2(\text{H}_2\text{O})_2^{2-}$
= $2[\text{ZnS}(\text{HS})\text{H}_2\text{O}]^-$

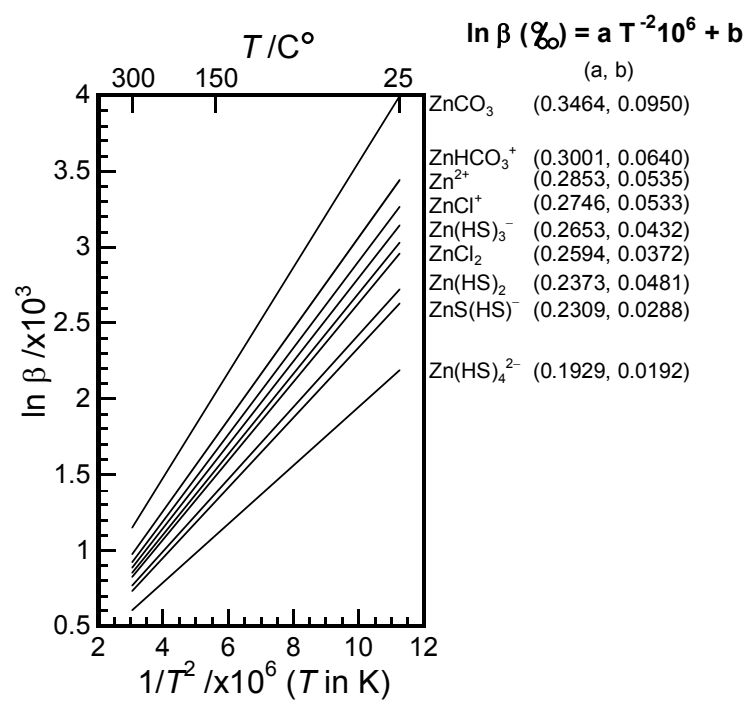


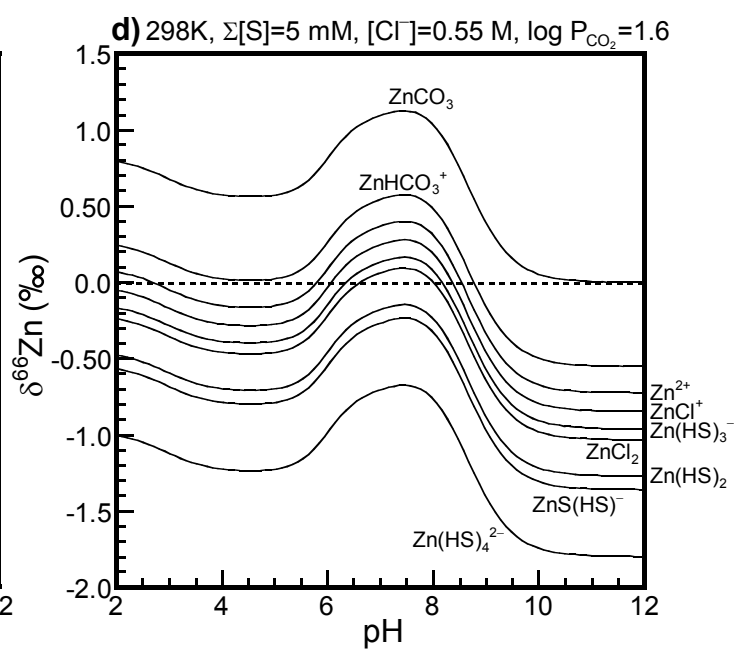
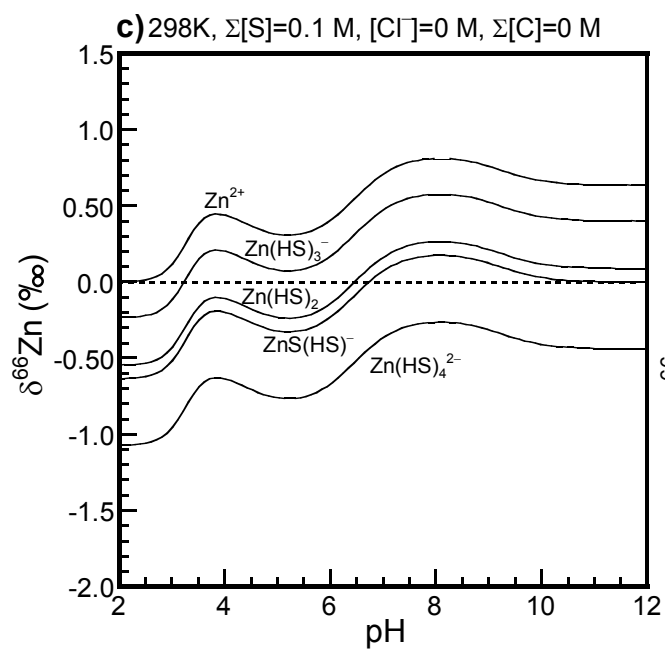
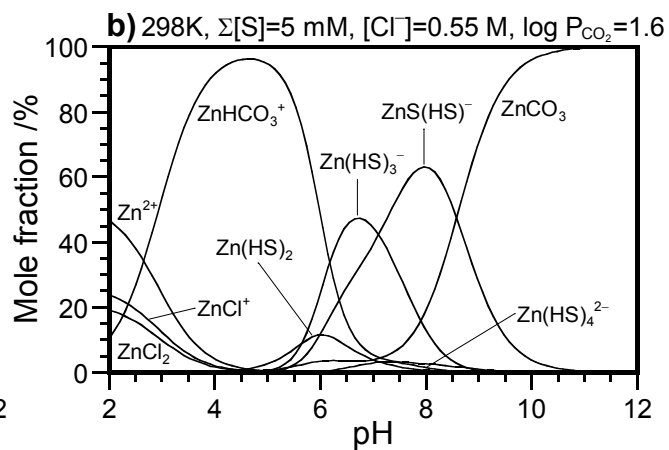
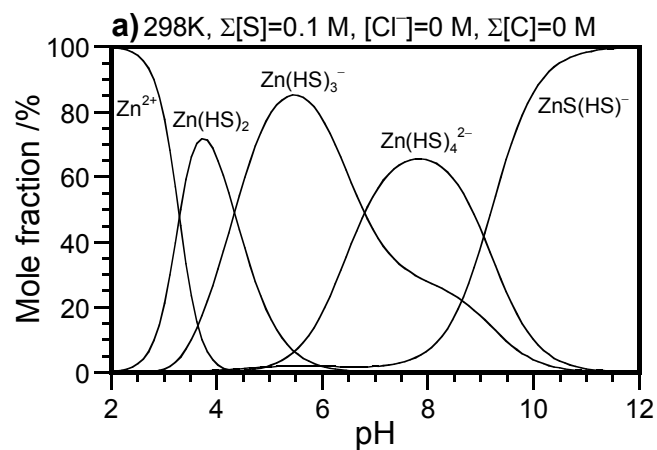
f) $\text{ZnHCO}_3(\text{H}_2\text{O})_4^+$

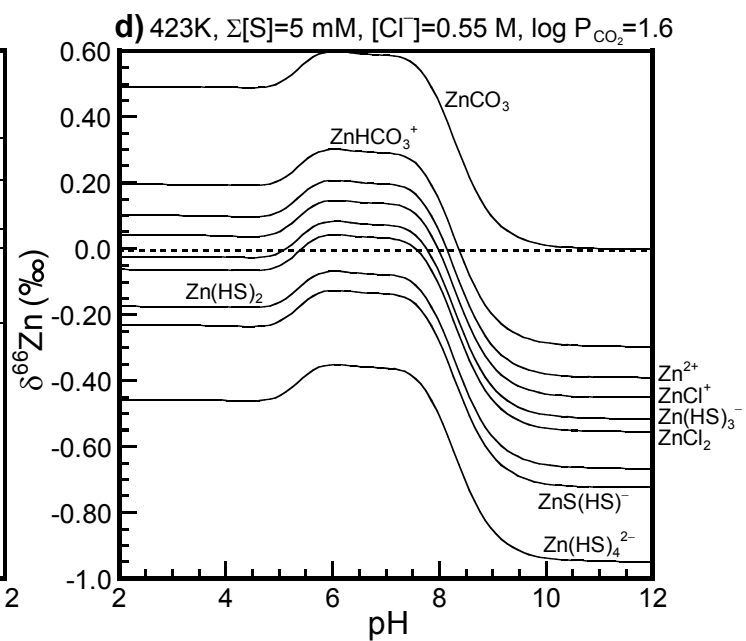
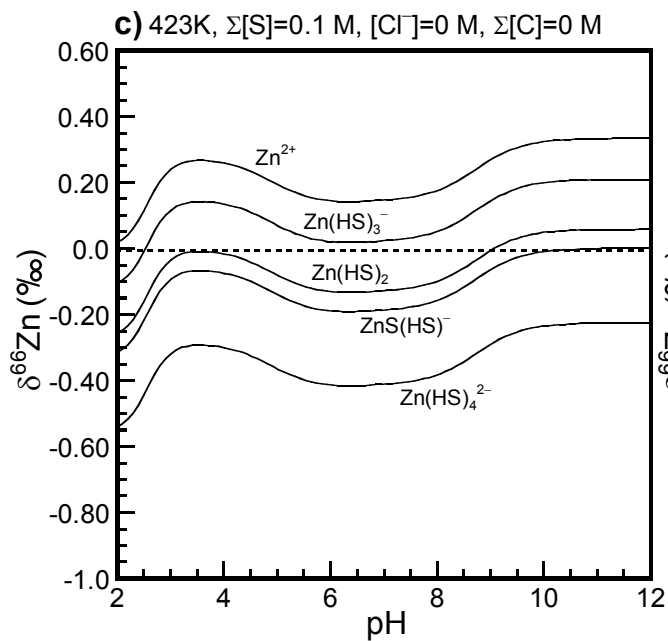
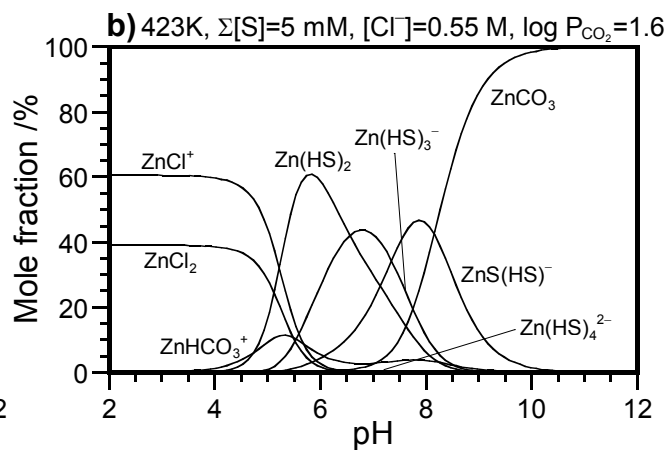
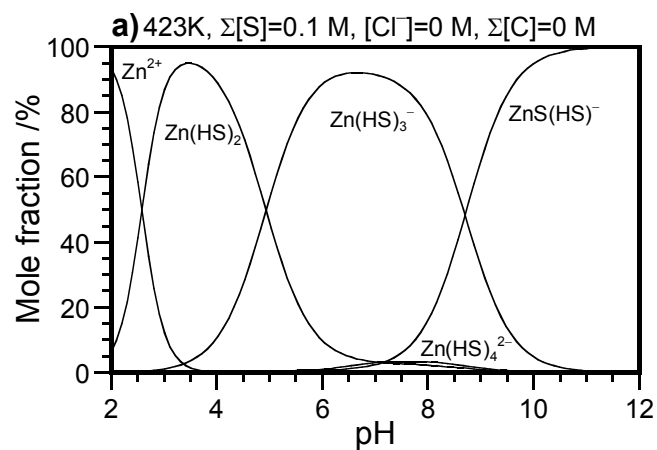


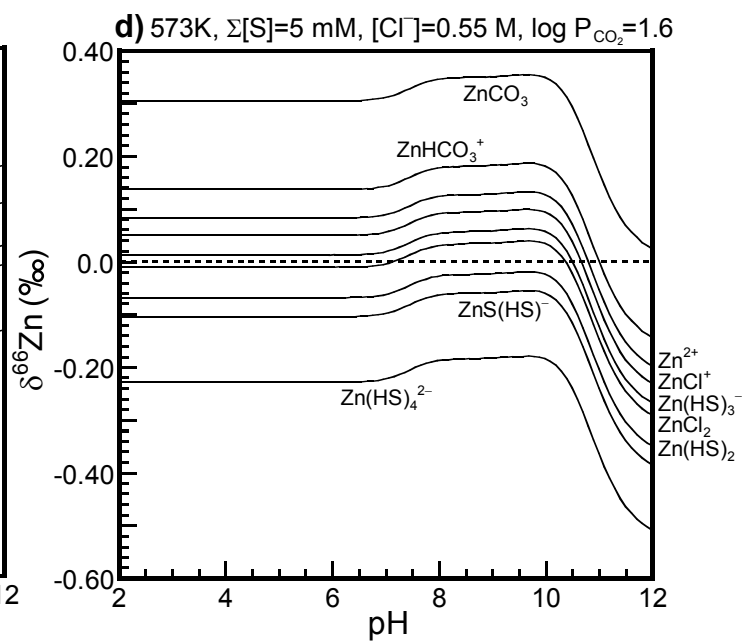
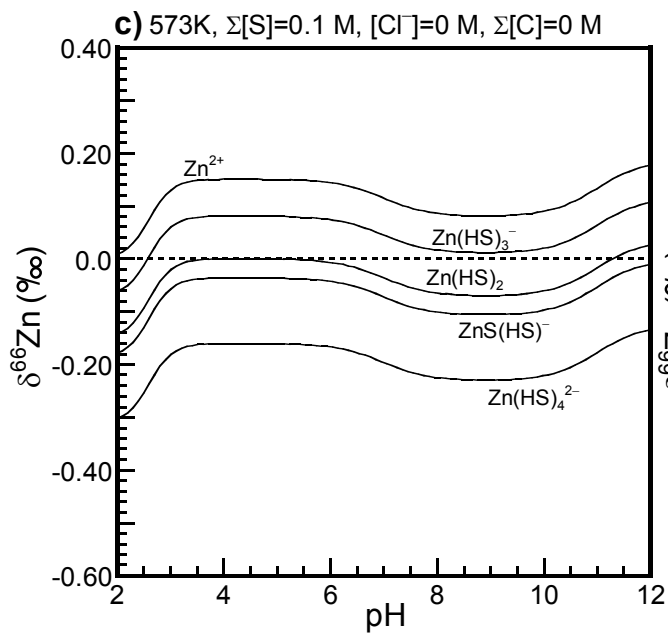
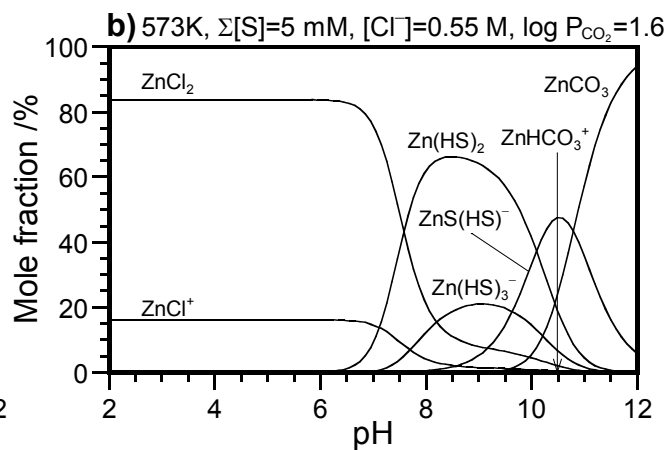
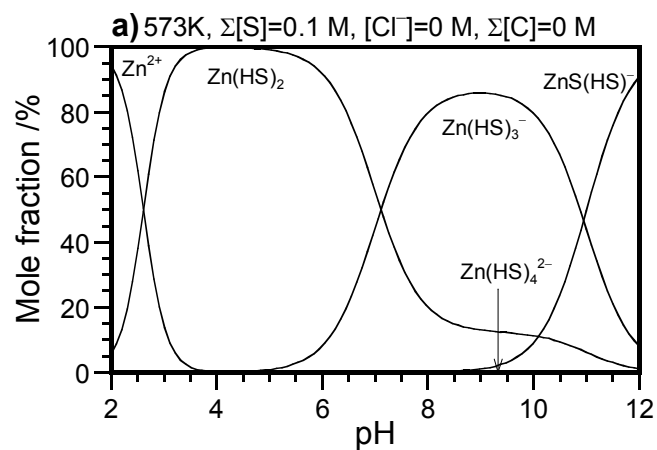
g) $\text{ZnCO}_3(\text{H}_2\text{O})_4$











Supplementary material

The origin of Zn Isotope Fractionation in Sulfides

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In order of appearance:

Figure S1: $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ with T_h symmetry and its vibrational modes, ν_1 , ν_2 , and ν_3

Table S1: Zn-O and O-H bond lengths and $\angle\text{HOH}$ angles

Table S2: ν_1 , ν_2 , and ν_3 frequencies

Table S3: $\ln \beta$'s at 298 K

Figure S2: Mole fractions of Zn species and Zn isotopic variations as functions of pH at 573 K (for stronger complexation of Zn carbonates).

Figure S3: Mole fractions of Zn species and Zn isotopic variations as functions of pH at 298 K ($\Sigma[\text{S}] = 0.1 \text{ M}$, $[\text{Cl}^-] = 0.55 \text{ M}$, and $\Sigma[\text{C}] = 0 \text{ M}$).

Figure S4: Mole fractions of Zn species and Zn isotopic variations as functions of pH at 423 K ($\Sigma[\text{S}] = 0.1 \text{ M}$, $[\text{Cl}^-] = 0.55 \text{ M}$, and $\Sigma[\text{C}] = 0 \text{ M}$).

Figure S5: Mole fractions of Zn species and Zn isotopic variations as functions of pH at 573 K ($\Sigma[\text{S}] = 0.1 \text{ M}$, $[\text{Cl}^-] = 0.55 \text{ M}$, and $\Sigma[\text{C}] = 0 \text{ M}$).

Figure S6: Mole fractions of Zn species and Zn isotopic variations as functions of pH at 298 K ($\Sigma[\text{S}] = 10 \text{ }\mu\text{M}$, $[\text{Cl}^-] = 0.55 \text{ M}$, and $\log P_{\text{CO}_2} = -3.4$).

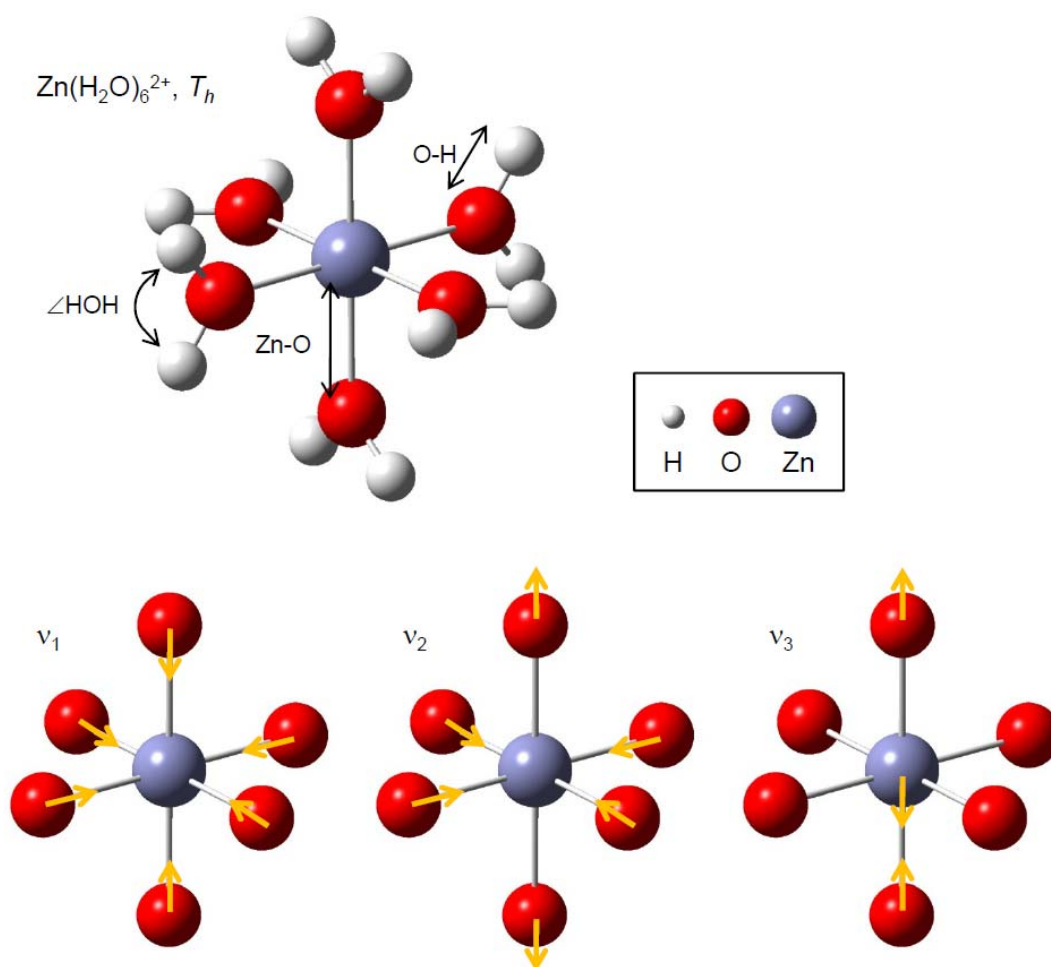


Fig. S1 $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ with T_h symmetry and its vibrational modes, ν_1 , ν_2 , and ν_3 . Structures are drawn by using GaussView3.0 (Gaussian Inc.).

Table S1
Zn-O and O-H bond lengths and \angle HOH angles

Theory/Basis sets ^a	Zn-O (Å)	O-H (Å)	\angle HOH (°)
B3LYP			
6-31G(d)	2.094	0.973	107.2
6-31G(d,p)	2.092	0.969	107.4
6-31+G(d)	2.124	0.974	107.4
6-31+G(d,p)	2.125	0.970	107.6
6-31++G(d,p)	2.125	0.970	107.6
6-311G(d)	2.095	0.965	108.4
6-311G(d,p)	2.097	0.966	107.3
6-311+G(d)	2.118	0.966	108.2
6-311+G(d,p)	2.128	0.967	107.4
6-311++G(d,p)	2.128	0.967	107.4
LanL2DZ & 6-31G(d)	2.131	0.973	107.1
LanL2DZ & 6-31G(d,p)	2.131	0.968	107.1
LanL2DZ & 6-31+G(d)	2.143	0.974	107.1
LanL2DZ & 6-31+G(d,p)	2.145	0.970	107.3
LanL2DZ & 6-31++G(d,p)	2.146	0.970	107.3
LanL2DZ & 6-311G(d)	2.131	0.965	108.3
LanL2DZ & 6-311G(d,p)	2.138	0.966	107.1
LanL2DZ & 6-311+G(d)	2.135	0.966	108.0
LanL2DZ & 6-311+G(d,p)	2.146	0.967	107.1
LanL2DZ & 6-311++G(d,p)	2.146	0.967	107.1
UHF			
LanL2DZ & 6-31G(d)	2.142	0.954	107.3

^a Orbital geometries and vibrational frequencies of aqueous Zn(II) species were computed using density functional theory (DFT) as implemented by the Gaussian03 code (Frisch et al., 2003). The DFT method employed here is a hybrid density functional consisting of Becke's three-parameter non-local hybrid exchange potential (B3) (Becke, 1993) with Lee-Yang and Parr (LYP) (Lee et al., 1988) non-local functionals. 6-31G and 6-311G basis set, which are all-electron basis sets, were chosen for H, O, and Zn. For comparison, an effective-core potential (ECP) basis set, LanL2DZ (Hay and Wadt, 1985a, b; Wadt and Hay, 1985), was tested for Zn. Unrestricted Hartree-Fock (UHF) theory was also tested.

Table S2
 ν_1 , ν_2 , and ν_3 frequencies

Theory/Basis sets	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})
B3LYP			
6-31G(d)	361	236	295
6-31G(d,p)	361	235	300
6-31+G(d)	336	217	290
6-31+G(d,p)	334	215	289
6-31++G(d,p)	335	216	289
6-311G(d)	372	246	339
6-311G(d,p)	371	244	334
6-311+G(d)	340	228	308
6-311+G(d,p)	333	219	294
6-311++G(d,p)	333	219	294
LanL2DZ & 6-31G(d)	338	243	301
LanL2DZ & 6-31G(d,p)	338	243	309
LanL2DZ & 6-31+G(d)	327	234	306
LanL2DZ & 6-31+G(d,p)	325	231	304
LanL2DZ & 6-31++G(d,p)	325	231	304
LanL2DZ & 6-311G(d)	342	250	329
LanL2DZ & 6-311G(d,p)	337	245	319
LanL2DZ & 6-311+G(d)	335	244	323
LanL2DZ & 6-311+G(d,p)	328	236	311
LanL2DZ & 6-311++G(d,p)	328	236	311
UHF			
LanL2DZ & 6-31G(d)	336	234	309

Table S3:
ln β 's at 298 K

Theory/Basis sets	ln β (‰)
B3LYP	
6-31G(d)	3.427
6-31G(d,p)	3.405
6-31+G(d)	3.274
6-31+G(d,p)	3.215
6-31++G(d,p)	3.214
6-311G(d)	4.190
6-311G(d,p)	4.044
6-311+G(d)	3.501
6-311+G(d,p)	3.250
6-311++G(d,p)	3.239
LanL2DZ & 6-31G(d)	3.753 (3.74 ^a)
LanL2DZ & 6-31G(d,p)	3.732
LanL2DZ & 6-31+G(d)	3.520
LanL2DZ & 6-31+G(d,p)	3.465
LanL2DZ & 6-31++G(d,p)	3.474
LanL2DZ & 6-311G(d)	4.085
LanL2DZ & 6-311G(d,p)	3.838
LanL2DZ & 6-311+G(d)	3.859
LanL2DZ & 6-311+G(d,p)	3.600
LanL2DZ & 6-311++G(d,p)	3.598
UHF	
LanL2DZ & 6-31G(d)	3.594 (3.58 ^a)

^a Black et al. (2011)

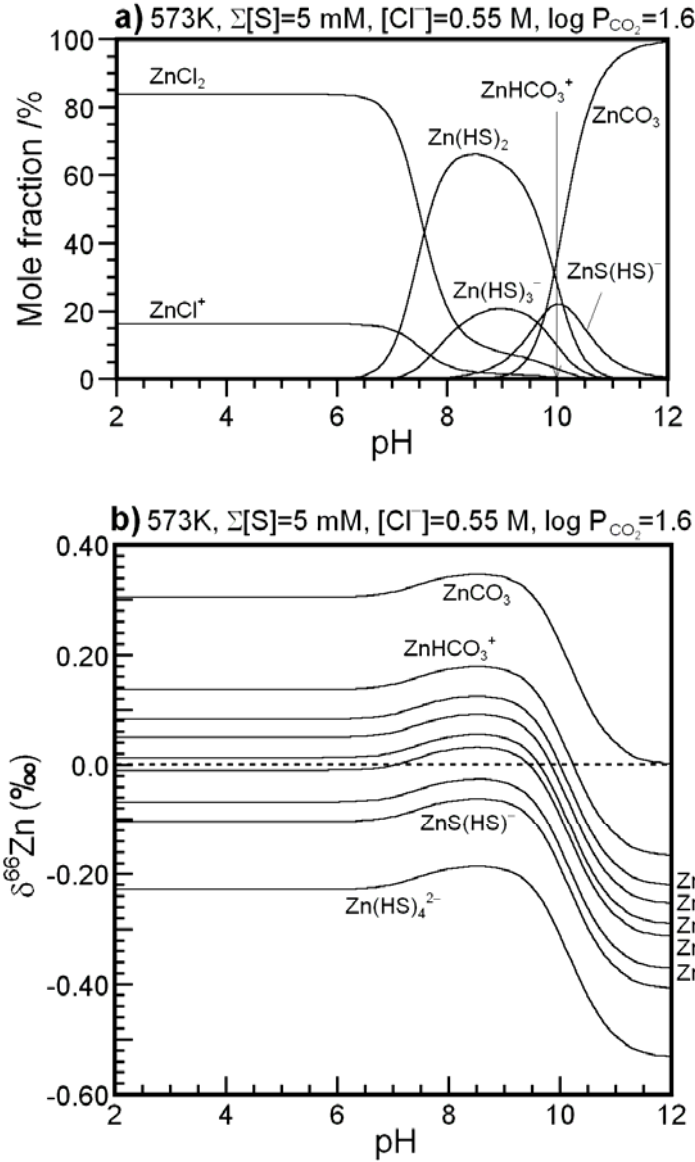


Fig. S2. Mole fractions of Zn species and Zn isotopic variations as functions of pH at 573 K (for stronger complexation of Zn carbonates). a) Mole fractions of Zn species with $\Sigma[S]=5$ mM and $[Cl^-] = 0.55$ M under $P_{CO_2} = 50$ bar, b) $\delta^{66}Zn$ under the hydrothermal condition. Under an assumption that formations of $ZnHCO_3^+$ and $ZnCO_3$ are enhanced by increasing temperature, $K_{ZnHCO_3^+}$ and K_{ZnCO_3} were multiplied by 10 (as an example) and $\log K_{ZnHCO_3^+} = 3.1$ and $\log K_{ZnCO_3} = 6.3$ were used. Mole fraction of Zn^{2+} in Fig. S2b is smaller than 0.001%. The maximum value of $Zn(HS)_4^{2-}$ mole fraction is 0.0002% at pH=9.3. The maximum value of $ZnHCO_3^+$ mole fraction is 0.5% at pH= 10.0. Dotted line in b) means $\delta^{66}Zn$ of bulk solution (averaged $\delta^{66}Zn$ in the whole solution). $\Sigma[Zn]$ was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).

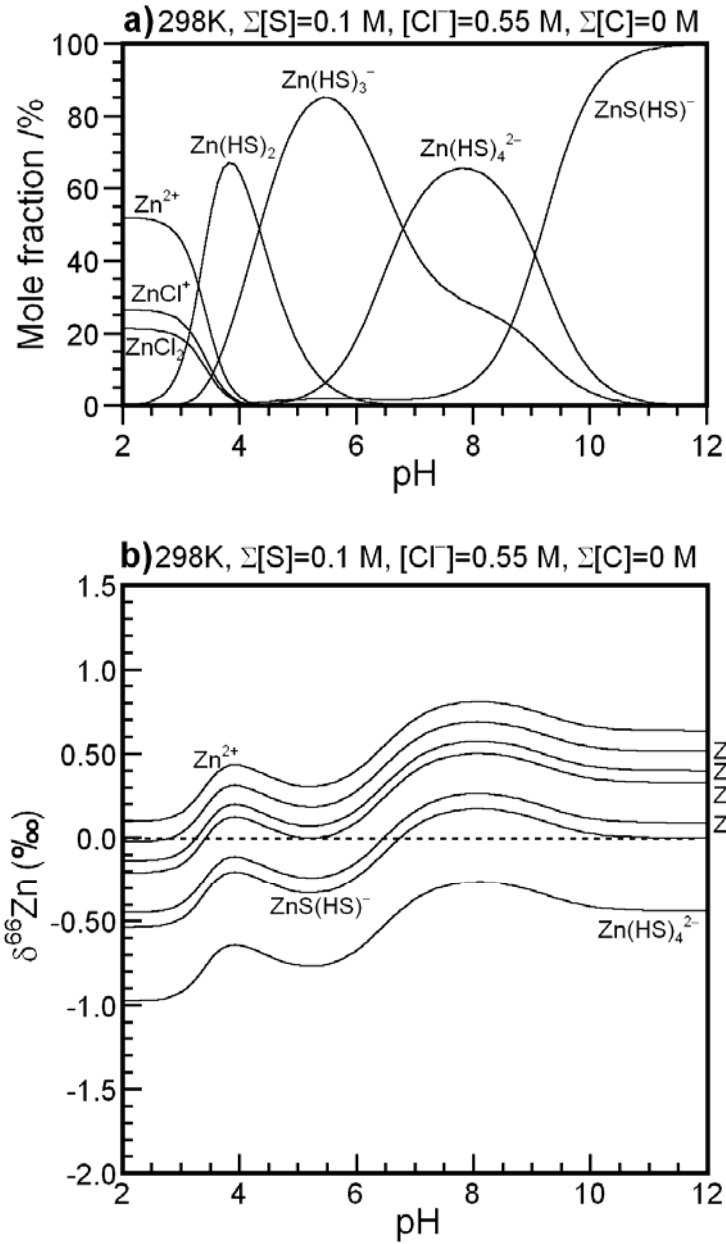


Fig. S3

Mole fractions of Zn species and Zn isotopic variations as functions of pH at 298 K ($\Sigma[S] = 0.1$ M, $[Cl^-] = 0.55$ M, and $\Sigma[C] = 0$ M). a) Mole fractions of Zn species in carbonate free hydrous fluid under $\Sigma[S]=0.1$ M and $[Cl^-] = 0.55$ M, b) $\delta^{66}\text{Zn}$ in carbonate free hydrous fluid. Dotted line in b) means $\delta^{66}\text{Zn}$ of bulk solution (averaged $\delta^{66}\text{Zn}$ in the whole solution). $\Sigma[\text{Zn}]$ was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).

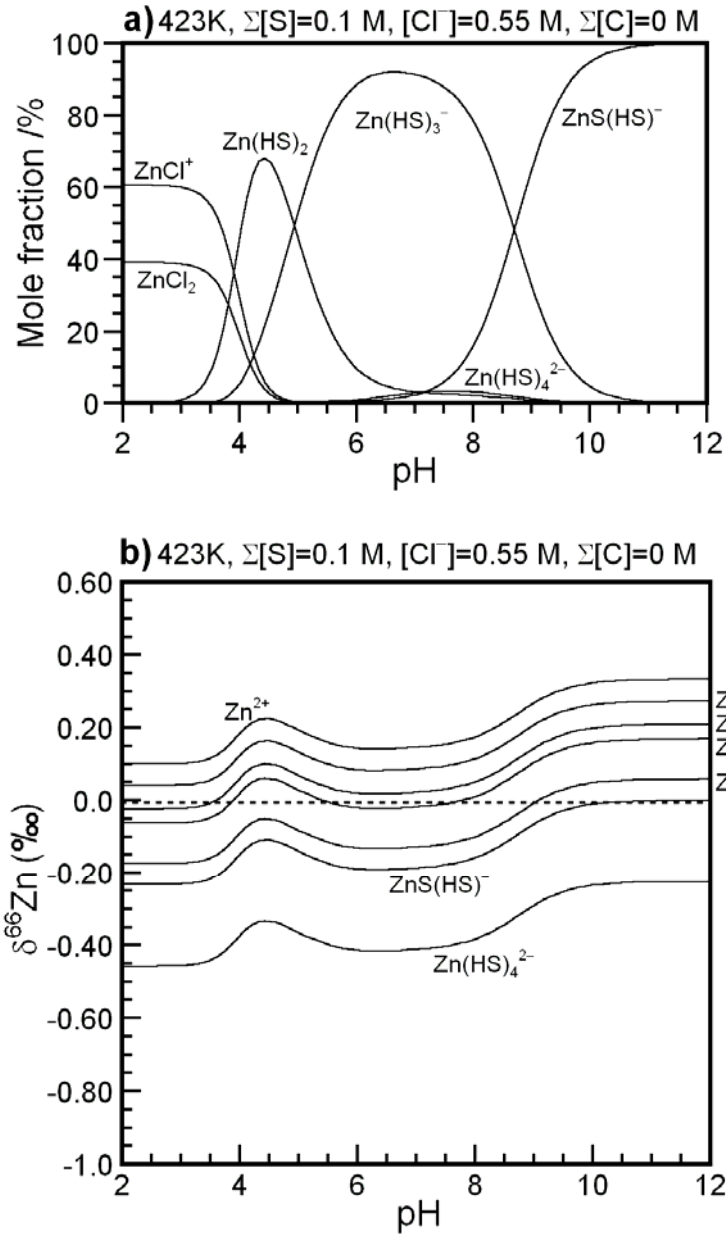


Fig. S4

Mole fractions of Zn species and Zn isotopic variations as functions of pH at 423 K ($\Sigma[S] = 0.1$ M, $[Cl^-] = 0.55$ M, and $\Sigma[C] = 0$ M). a) Mole fractions of Zn species in carbonate free hydrous fluid under $\Sigma[S]=0.1$ M and $[Cl^-] = 0.55$ M, b) $\delta^{66}Zn$ in carbonate free hydrous fluid. Mole fraction of Zn^{2+} is 0.14% at pH=2 and smaller than that at pH>2. Dotted line in b) means $\delta^{66}Zn$ of bulk solution (averaged $\delta^{66}Zn$ in the whole solution). $\Sigma[Zn]$ was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).

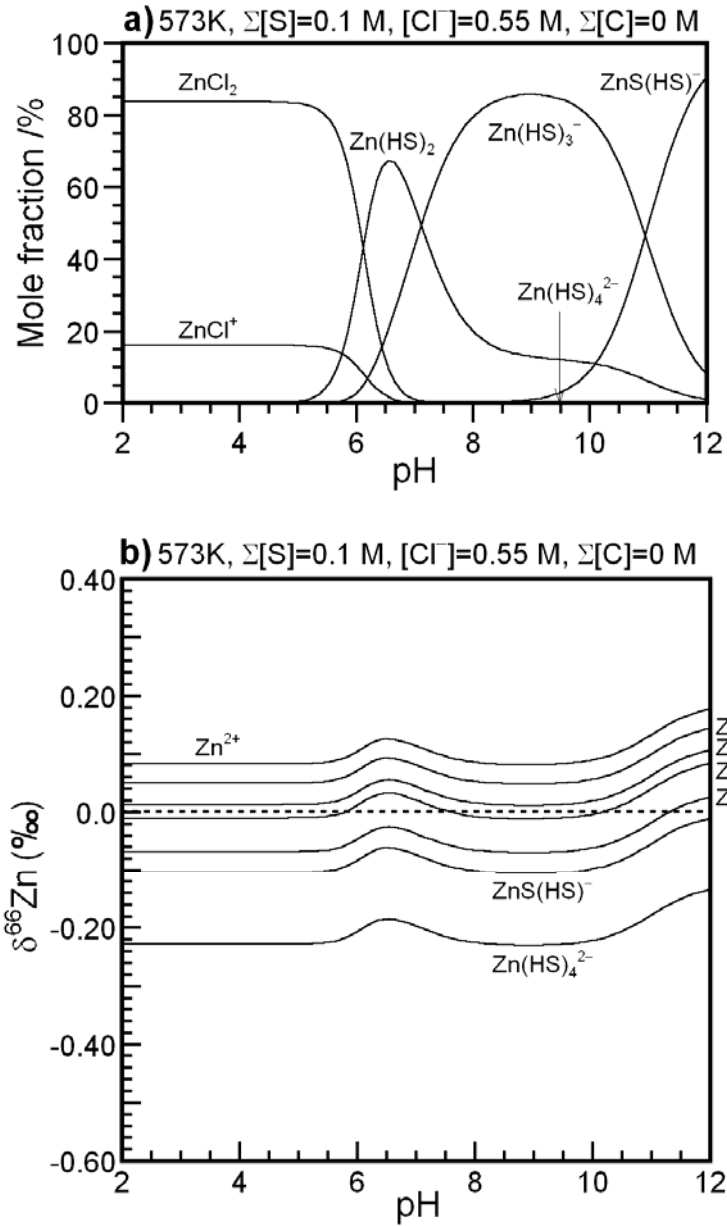


Fig. S5

Mole fractions of Zn species and Zn isotopic variations as functions of pH at 573 K ($\Sigma[S] = 0.1$ M, $[Cl^-] = 0.55$ M, and $\Sigma[C] = 0$ M). a) Mole fractions of Zn species in carbonate free hydrous fluid under $\Sigma[S]=0.1$ M and $[Cl^-] = 0.55$ M, b) $\delta^{66}\text{Zn}$ in carbonate free hydrous fluid. Mole fraction of Zn^{2+} is smaller than 0.001%. The maximum value of $\text{Zn}(\text{HS})_4^{2-}$ mole fraction is 0.02% at pH=9.5. Dotted line in b) means $\delta^{66}\text{Zn}$ of bulk solution (averaged $\delta^{66}\text{Zn}$ in the whole solution). $\Sigma[\text{Zn}]$ was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).

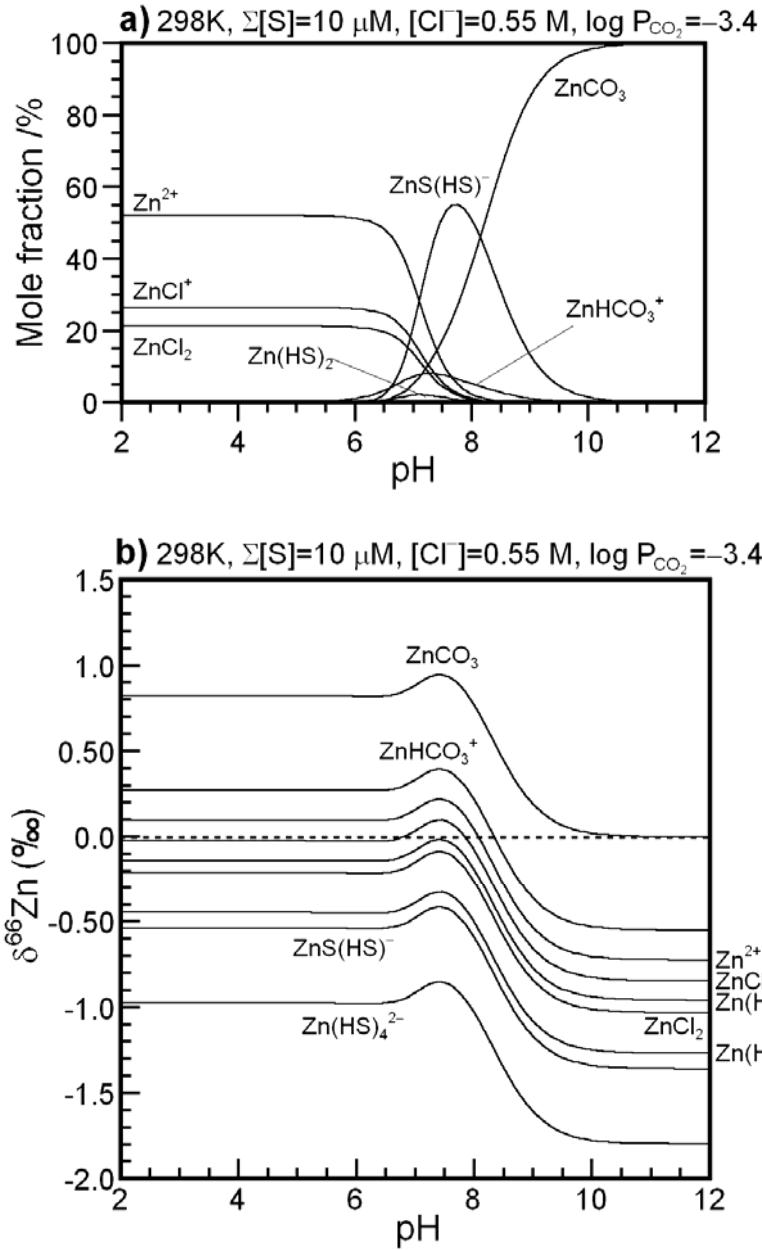


Fig. S6

Mole fractions of Zn species and Zn isotopic variations as functions of pH at 298 K ($\Sigma[S] = 10 \mu\text{M}$, $[\text{Cl}^-] = 0.55 \text{ M}$, and $\log P_{\text{CO}_2} = -3.4$). a) Mole fractions of Zn species in hydrous fluid under low $\Sigma[S]$ and P_{CO_2} condition, b) $\delta^{66}\text{Zn}$ in the hydrous fluid. $\Sigma[S]$ and P_{CO_2} were set much smaller than those of Figs. 3a and 3c. The maximum value of $\text{Zn}(\text{HS})_3^-$ mole fraction is 0.06% at $\text{pH}=7.3$. The maximum value of $\text{Zn}(\text{HS})_4^{2-}$ mole fraction is 0.00001% at $\text{pH}=7.4$. Dotted line in b) means $\delta^{66}\text{Zn}$ of bulk solution (averaged $\delta^{66}\text{Zn}$ in the whole solution). $\Sigma[\text{Zn}]$ was set to be $10^{-6.1} \text{ M}$ (Tagirov and Seward, 2010).

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