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# First-principles calculation of Zn isotope fractionation during internal adsorption of soil organic matter

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### ABSTRACT

Zn is one of the main ore-forming elements and has important economic value. However, as a heavy metal element, excessive emission will cause serious environmental pollution. At the same time, Zn is a trace element needed for life activities, which is an important component of a variety of enzymes or coenzymes in organisms, and has great significance for biological life activities. But in high concentrations it becomes toxic and affects the health of the organism. This study is based on the first-principles calculation method of density functional theory (DFT) to accurately quantify Zn isotope balance fractionation during the internal formation of organic matter. The calculated results are as follows:  $\Delta^{66/64}\text{Zn} = -0.232 \sim -3.036\text{‰}$  at 25 °C. The more N and S atoms present in the donor atom, the greater the equilibrium fractionation and the greater the enrichment of lighter Zn isotopes.

**Keywords:** Zn isotope, isotopic fractionation, organic matter, first principle calculations

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## Introduction

With the rapid development of industry, agriculture and mining production, the heavy metal pollution of soil is more and more serious in our country. According to the National Soil Pollution Survey Bulletin jointly issued by the Ministry of Environmental Protection and the Ministry of Land and Resources in 2014, the country's soil environment is not optimistic on the whole. Soil pollution is serious in some areas, soil environmental quality of cultivated land is worrying, and soil environmental problems of abandoned industrial and mining lands are particularly prominent. Most Zn pollution occurs in Fujian Province, the south of China. The types of pollutants include inorganic pollutants and organic pollutants. Inorganic pollutants mainly consist of 8 heavy metals, cadmium, mercury, arsenic, copper, lead, chromium, zinc and nickel, and their exceedance points account for 82.8% of all the exceedance points. Organic pollution followed; compound pollution was the least.

Zinc (Zn), as a transitional metal element with atomic number 30, has an abundance of about 71 µg/g in the Earth's crust, which is a common metal next to iron, Cu and Al [1,2]. Zn has five stable isotopes,  $^{64}\text{Zn}$ ,  $^{66}\text{Zn}$ ,  $^{67}\text{Zn}$ ,  $^{68}\text{Zn}$  and  $^{70}\text{Zn}$ , and their abundance is 48.63%, 27.90%, 4.10%, 18.75% and 0.62%, respectively. The average relative atomic mass is 65.37777 [3]. The isotopic composition of Zn is usually expressed as  $\delta^{66}\text{Zn}$ , defined as the thousandth deviation from the  $^{66}\text{Zn}$ - $^{64}\text{Zn}$  ratio of the sample to the standard sample [4]:  $\delta^{66}\text{Zn}=[(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}} / (^{66}\text{Zn}/^{64}\text{Zn})_{\text{standard sample}} - 1] \times 1000$ . Due to the large mass difference between  $^{64}\text{Zn}$  and  $^{66}\text{Zn}$  isotopes, significant isotopic fractionation occurs in most physicochemical processes under superbiogenic conditions. At the same time, Zn is also an indispensable trace element in biological life activities and plays an important role in biological life

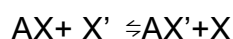
activities. Some scholars have used the ratio of  $^{66}\text{Zn}/^{64}\text{Zn}$  as a geochemical and biochemical tracer [4] or a medical marker [5]. In terms of Marine geochemistry, Bermin et al [6] measured the variation of the  $^{66}\text{Zn}/^{64}\text{Zn}$  ratio in the depth profile of the Northeast Pacific Ocean to detect and quantify paleomarine environmental conditions. In terms of environmental science, when tracing the sources of Zn, Chen et al [7] and Borrok et al [8] found that the isotopic composition of Zn in the source sources was significantly different from that of natural sources and used the isotopic composition of Zn to trace the source sources and identify the sources of pollutants. In addition, Borrok [9] and Balistrieri [10] also used Zn isotopes to characterize Zn in rivers from various geological Settings and to identify biogeochemical processes affecting the distribution of the element. In terms of mineral deposit science, Zn isotope composition of ores was measured by predecessors to determine the geodynamic mechanism that may be related to the genesis of ore deposits [11]. In the aspect of cosmic chemistry, scholars have carried out Zn isotope analysis on chondrite and iron meteorites, found that different types of meteorites have different Zn isotope compositions. The reason for this change is that there are other trace elements Mn and Ge which have similar volatilization as Zn in the meteorites. If these isotopic parameters are obtained, various physical and chemical processes in the formation of the solar system can be further evaluated [12].

Among the various simulation methods, the first principles method based on density functional theory (DFT) is widely used to calculate isotope fractionation coefficient, element partition coefficient and vibration spectrum. However, obtaining a stable geometry is a prerequisite for calculating these parameters. The harmonic frequency required to calculate the isotopic fractionation

coefficient is the second partial derivative of the electron energy of the system with respect to its atomic coordinates.

## 1. Theory and method

In this study, first principal calculations were used to optimize the geometric configurations of the molecular clusters. BP86 was used as the exchange-correlation functional. The mixed basis sets were used to describe the wave function of the system, that is, LanL2MB for Cd and 6-311G (d) all-electron basis [13,14] for H, O, N, and S. When geometric optimization was completed, we checked the existence of imaginary vibrational frequencies of each configuration to confirm whether this configuration corresponded to a local minimum on the potential energy surface. Gaussian09/ Gaussian16 software was used to



$X'$  represents an ideal single-atom gas with heavy isotopes,  $X$  represents an ideal single-atom gas with light isotopes,  $AX$  represents a compound with light isotopes, and  $AX'$

$$K = \frac{Q_{trans}^{AX} Q_{rot}^{AX} Q_{vib}^{AX} Q_{elec}^{AX}}{Q_{trans}^{AX'} Q_{rot}^{AX'} Q_{vib}^{AX'} Q_{elec}^{AX'}} \cdot \frac{Q_{trans}^X Q_{elec}^X}{Q_{trans}^{X'} Q_{elec}^{X'}} \quad (2)$$

$Q_{trans}$  represents the translational partition function,  $Q_{rot}$  the rotational partition function,  $Q_{vib}$  the vibrational partition function, and  $Q_{elec}$  the electronic partition function, respectively. For light elements, because the difference in the ground-state electron energy of the compound

$$Q_{trans} = V \left( \frac{2\pi M k T}{h^2} \right)^{3/2} \quad (3)$$

$$Q_{rot} = \frac{\pi^{1/2} (8\pi^2 k T)^{3/2} (I_A I_B I_C)^{1/2}}{\sigma h^3} \quad (4)$$

$$Q_{vib} = \prod_i \frac{e^{-u_i/2}}{1 - e^{-u_i}} \quad (5)$$

Where  $V$  is the volume,  $M$  is the mass,  $m$  is the mass of atoms,  $I_A$  is the moment of inertia of axis  $A$  of rotation, and  $\sigma$  is the number of symmetrical molecules,  $u_i = hc\omega_i/kT$ , where  $h$  is Planck's constant,  $k$  is the Boltzmann constant,

calculate the electronic energy and harmonic vibrational frequency of the system [15,16].

## 1.1 Calculation of equilibrium fractionation factor

Urey [17] and Bigeleisen and Mayer [18] described a scenario of isotope exchange between a compound and ideal single-atom gas. They proposed an important parameter, the reduced partition function ratio (RPFR), to quantify the relative enrichment of heavy isotopes in compounds. The parameter value mainly depends on the harmonic vibrational frequency of the compound before and after isotope substitution. RPFR value is greater than 1, the greater the degree of heavy isotope enrichment in a given substance.

For isotope exchange reactions between the compound and ideal single-atom gas,

$$(1)$$

represents a compound with heavy isotopes.

The equilibrium constant of this reaction can be expressed as:

before and after isotope substitution is indistinguishable, the contribution of the electron partition function to the RPFR value can be ignored. Specifically, the translational partition function, rotational partition function, and vibration partition function can be expressed as:

$T$  is the absolute temperature (K),  $c$  is the speed of light, and  $\omega$  is the harmonic vibrational frequency in  $\text{cm}^{-1}$  [19]. Using the Teller-Redlich [20] formula for further approximation, we obtain:

$$\left(\frac{M}{M}\right)_{AX}^{3/2} \left(\frac{I_A I_B I_C}{I_A I_B I_C}\right)_{AX}^{1/2} \left(\frac{m}{m}\right)_X^{3n/2} = \prod_i \frac{u_i}{u_i} \quad (6)$$

Finally, both the translational partition function ratio and rotational partition function ratio can be expressed in terms of vibrational frequency.

Through a series of mathematical transformations, the partition function ratio (RPFR (AX/AX')) is defined as follows:

$$\text{RPFR}_{(AX/AX')} = \frac{\sigma}{\sigma'} K = \prod_i \frac{u_i}{u_i'} \left( \frac{e^{-\frac{u_i}{2}}}{e^{-\frac{u_i'}{2}}} \right) \left( \frac{1 - e^{-u_i}}{1 - e^{-u_i'}} \right) \quad (7)$$

The RPFR value is equivalent to  $\beta$ , a factor commonly used in the chemistry community, i.e., the isotope fractionation factor between compounds and ideal single-atom gases [21]. When the

RPFRs of phases A and B at equilibrium are known, the isotopic fractionation factor  $\alpha$  can be expressed as the ratio of their RPFRs (or  $\beta$  factors):

$$\alpha_{A-B} = \frac{\text{RPFR}_A}{\text{RPFR}_B} = \frac{\beta_A}{\beta_B} \quad (8)$$

The equilibrium isotope fractionation values between the two phases were calculated using the formula  $\Delta_{A-B} = \delta_A - \delta_B \approx 1000 (\ln \beta_A - \ln \beta_B) = 1000 \ln \alpha_{A-B}$ . This formula connects theoretical calculations and experimental determinations and is convenient for comparing isotope

fractionation data.

At the same time, the RPFR platform value of each Cd-containing species was confirmed by using the minimum root-mean-square error (RMSE) method [22]:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (X - Y)^2}{n}} \quad (9)$$

Where X represents each RPFR value we calculated, and Y is the expected plateau value. The RMSE value changes with the change in the Y value, and the Y value corresponding to the minimum RMSE value is the plateau value of a Cd-containing species.

## 1.2 Construction of molecular cluster model

Although some studies have shown that the structures capable of complexing metal ions in the structure of organic matter are mainly oxygen-containing functional groups, such as hydroxyl and carboxyl groups, at the same time, N and S in organic matter can also be complexed with metals as donor atoms. Based on the previous models in X-ray single crystal diffraction data or neutron diffraction data, we modify and reconstruct them. From this, the metal-organic framework (MOFs) is constructed. Zinc enters the interior of organic lattices, and it is assumed that

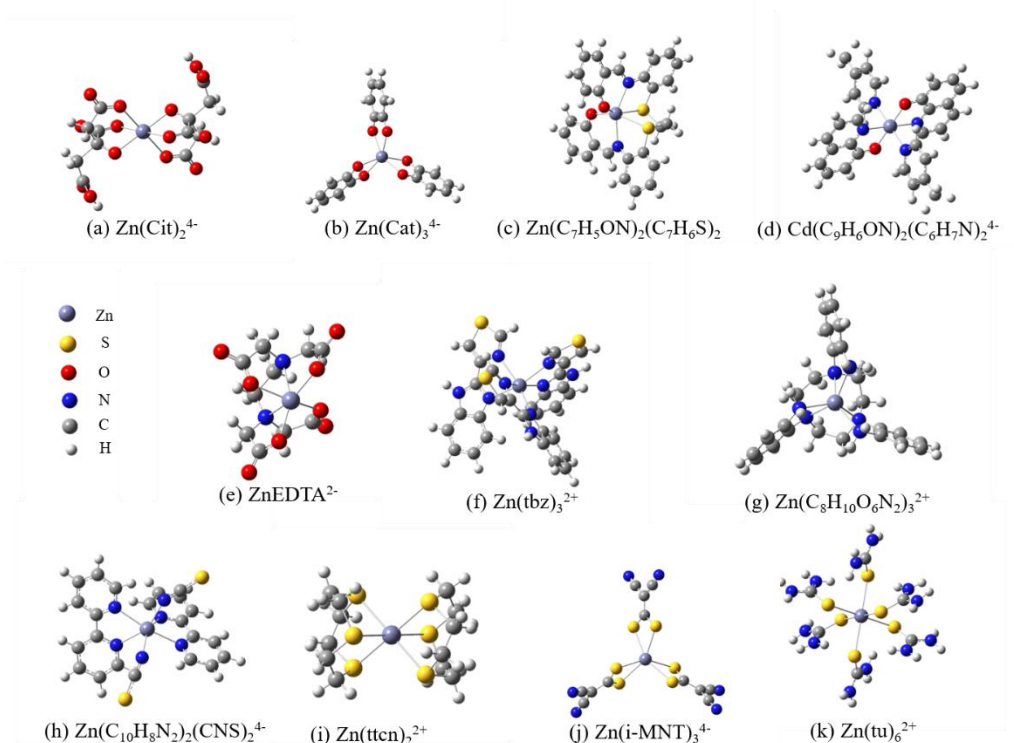
there are not many water molecules around  $\text{Zn}^{2+}$ . The case of organic ligands with different combinations of hydroxyl, carboxyl, N and S atoms is also considered in the MOFs configuration.

## 2. Results and discussion

### 2.1 Zn enters the internal geometry of organic matter

Humus is a kind of replicated polymer aromatic polymer, widely distributed in nature, with adsorption and chelation of heavy metal ions [23]. At present, the specific structure of humus has not been determined. However, the main functional groups that can adsorb and complex metal cations on its surface are clear, including phenolic hydroxyl group, carboxyl group, carbon group, etc. In this paper, 11 kinds of organic matter were selected, and the configuration of Zn entering into the organic matter was optimized. The configuration of the optimized metal entering into the

organic matter was shown in Fig. 1.



**Fig. 1** Zn enters the internal geometry of organic matter.

## 2.2 Isotopic equilibrium fractionation

Based on the RPFR value of  $\text{Zn}^{2+}$  aqueous solution, we calculated the equilibrium fractionation value of Zn isotope between organic matter and

aqueous solution at  $25^\circ\text{C}$ , as shown in Table 1. Studies have shown that the type of donor atom of organic ligand can affect the equilibrium fractionation of Zn isotope [24].

**Table 1** Equilibrium isotope fractionation between Zn-containing species and aqueous solutions

species	$1000 \ln \beta$ (‰, $25^\circ\text{C}$ )	Zn-N\Zn-S**\Zn-O*** bond length (Å)	$\Delta^{66/64}\text{Zn}$ (‰, $25^\circ\text{C}$ )
Zn(Cat) $_3^{4-}$	1.223	2.243***	-1.559
Zn(cit) $_2^{4-}$	1.346	2.240***	-1.274
Zn(C $_7$ H $_5$ ON) $_2$ (C $_7$ H $_6$ S) $_2$	1.577	2.192*, 2.783**, 2.023***	-0.742
Zn(C $_9$ H $_6$ ON) $_2$ (C $_6$ H $_7$ N) $_2^{4-}$	1.739	2.257*, 2.092***	-0.366
ZnEDTA $^{2-}$	1.798	2.315*, 2.141***	-0.232
Zn(tbz) $_3^{2+}$	1.501	2.244*	-0.918
Zn(C $_8$ H $_{10}$ O $_6$ N $_2$ ) $_3^{2+}$	1.688	2.261*	-0.484
Zn(C $_{10}$ H $_8$ N $_2$ ) $_2$ (CNS) $_2^{4-}$	1.635	2.208*	-0.607
Zn(ttcn) $_2^{2+}$	0.936	2.616**	-2.222
Zn(i-MNT) $_3^{4-}$	0.583	2.724**	-3.036
Zn(tu) $_6^{2+}$	0.645	2.690**	-2.892

## 3. Conclusions

For 11 Zn organic complexes, it can be seen

from Fig. 1 that the coordination number of central  $\text{Zn}^{2+}$  is all six-coordination, and it can be seen from Table 1 that the length of Zn-S and Zn-N bonds in the optimized configuration is significantly longer than that of Zn-O bonds. According to the calculated fractionation values, light Zn isotopes are relatively enriched when entering Zn into organic matter, especially when S donor atoms are more likely to enrich light Zn isotopes than O donor atoms. Since Zn and Cd are in the same group as the periodic table, they have similar chemical properties. Yang et al.<sup>[25]</sup> also showed that complexes containing S donor atoms are richer in light Cd isotopes than complexes containing O and N donor atoms. Zhao et al.<sup>[26]</sup> studied the theoretical isotope fractionation during the complexation of  $\text{Cd}^{2+}$  with organic ligand, which also showed that for Cd complexes, combinations containing S or S and O donor atoms tend to bind to lighter Cd isotopes. The difference of equilibrium fractionation values of different complexes indicates that the equilibrium fractionation values between organic matter containing Zn and aqueous solution during the chelation of organic matter with  $\text{Zn}^{2+}$  are affected by the type of donor atom. In general, organic ligands containing S donor atoms tend to enrich lighter Zn isotopes than those containing O or N and O donor atoms.

## Reference

- [1] Wang Z W, Yuan W, Cheng J B. A review of stable isotope geochemistry of Zn[J]. *Earth frontier*, 2015, 22(5):10.
- [2] Paniello R C D J M, Moynier F. Zinc isotopic evidence for the origin of the Moon[J]. *Nature*, 2012, 490: 376-379.
- [3] Moynier F, Vance D, Fujii T, et al. 13 The Isotope Geochemistry of Zinc and Copper[J].
- [4] Maréchal C, Télouk P, Albarède F. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry[J]. *Chemical Geology*, 1999, 156(1-4): 251-273.
- [5] Ingle C P, Langford N, Harvey L J, et al. Comparison of three different instrumental approaches to the determination of iron and zinc isotope ratios in clinical samples[J]. *Journal of Analytical Atomic Spectrometry*, 2004, 19(3): 404-406.
- [6] Bermin J, Vance D, Archer C, et al. The determination of the isotopic composition of Cu and Zn in seawater[J]. *Chemical geology*, 2006(3-4): 226.
- [7] Chen J B, Gaillardet J, Louvat P, et al. Zn isotopes in the suspended load of the Seine River, France: Isotopic variations and source determination[J]. *Geochimica Et Cosmochimica Acta*, 2009, 73(14): 4060-4076.
- [8] Borrok D M, Wanty R B, Ridley W I, et al. Application of iron and zinc isotopes to track the sources and mechanisms of metal loading in a mountain watershed[J]. *Applied Geochemistry*, 2009, 24(7): 1270-1277.
- [9] Borrok D M, Nimick D A, Wanty R B, et al. Isotopic variations of dissolved copper and zinc in stream waters affected by historical mining[J]. *Geochimica Et Cosmochimica Acta*, 2008, 72(2): 329-344.
- [10] Balistrieri L S, Borrok D M, Wanty R B, et al. Fractionation of Cu and Zn isotopes during adsorption onto amorphous Fe(III) oxyhydroxide: Experimental mixing of acid rock drainage and ambient river water[J]. *Geochimica Et Cosmochimica Acta*, 2008, 72(2): 311-328.
- [11] Mason T, Weiss D J, Chapman J B, et al. Zn and Cu isotopic variability in the Alexandrinka volcanic-hosted massive sulphide (VHMS) ore deposit, Urals, Russia[J]. *Chemical Geology*, 2005, 221(3-4): 170-187.
- [12] Moynier F, Blichert-Toft J, Telouk P, et al. Comparative stable isotope geochemistry of Ni, Cu, Zn, and Fe in chondrites and iron

- meteorites[J]. *Geochimica Et Cosmochimica Acta*, 2007, 71(17): 4365-4379.
- [13] Ducher M, Blanchard M, Balan E. Equilibrium isotopic fractionation between aqueous Zn and minerals from first-principles calculations[J]. *Chemical Geology*, 2018: S0009254118301116.
- [14] Kavner A, John S G, Sass S, et al. Redox-driven stable isotope fractionation in transition metals: Application to Zn electroplating[J]. *Geochimica Et Cosmochimica Acta*, 2008, 72(7): 1731-1741.
- [15] Sivry Y, Riotte J, Sonke J E, et al. Zn isotopes as tracers of anthropogenic pollution from Zn-ore smelters The Riou Mort-Lot River system[J]. *Chemical Geology*, 2008, 255(3-4): 295-304.
- [16] Sonke J E, Sivry Y, Viers J, et al. Historical variations in the isotopic composition of atmospheric zinc deposition from a zinc smelter[J]. *Chemical Geology*, 2008, 252(3-4): 145-157.
- [17] Urey, Harold C. The thermodynamic properties of isotopic substances, I[J]. *J. Chem. Soc. (London)*, 1947: 562.
- [18] Bigeleisen J, Mayer M G. Calculation of Equilibrium Constants for Isotopic Exchange Reactions[J]. *Journal of Chemical Physics*, 1947, 15(5): 261-267.
- [19] Qi L, Tossell J A, Yun L. On the proper use of the Bigeleisen–Mayer equation and corrections to it in the calculation of isotopic fractionation equilibrium constants[J]. *Geochimica Et Cosmochimica Acta*, 2010, 74(24): 6965-6983.
- [20] O R. Eine allgemeine Beziehung zwischen den Schwingungsfrequenzen isotoper Molekeln[J]. *Zeitschrift für Physikalische Chemie*, 1935, 28(1): 11.
- [21] Richet P B Y, Janoy M. A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope enrichment among gaseous molecules[J]. *Annual Review of Earth and Planetary Sciences*, 1977, 5(1): 55.
- [22] W W M. Vibrational frequency prediction using density functional theory[J]. *Chemical Physics Letters*, 1996, 256(4-5): 8.
- [23] Ratié G, Chrastn V, Guinoiseau D, et al. Cadmium isotope fractionation during complexation with humic acid[J]. *Environmental Science & Technology*, 2021, in press.
- [24] Francis, Albarède, Philippe, et al. Isotopic evidence of unaccounted for Fe and Cu erythropoietic pathways[J]. *Metallomics : integrated biometal science*, 2011.
- [25] Yang J, Li Y, Liu S, et al. Theoretical calculations of Cd isotope fractionation in hydrothermal fluids[J]. *Chemical Geology*, 2015, 391: 74-82.
- [26] Yang Z A, Yi B, Mwc D, et al. Theoretical isotope fractionation of cadmium during complexation with organic ligands[J]. *Chemical Geology*, 2021.

