Research Article **AJBAS (2022) 5:25**

American Journal of Basic and Applied Sciences
(ISSN:2637-6857)

Ge isotopic equilibrium fractionation between Ge-containing ferrihydrite and the aqueous solution

Peng-dong Wang

School of Earth Science and Engineering, Hebei University of Engineering, Handan 056038, China.

ABSTRACT

Since Ge has a strong affinity for Fe, iron oxyhydroxide is assumed to be one of the potential "missing sinks" of Ge. Ferrihydrite is commonly found in soil and sediments and has a strong affinity for heavy metals. In this study, the first principle method based on density functional theory was used to optimize the geometry of Ge-containing ferrihydrites and H4GeO4 aqueous solution molecular clusters at B3LYP/6-311G(d) level. Solvation effects are treated by "water-droplet" method. Finally, at 298.15 K we obtained the Ge isotopic equilibrium fractionation between Ge-containing ferrihydrites and H4GeO4 aqueous solution, Δ74/70Geferrihydrite-aq= -1.97‰. It enriches the document of Ge isotopic fractionation and helps to assist the study of Ge global cycle.

Keywords: Ge isotopes; isotopic equilibrium fractionation; first-principles calculation; ferrihydrite

***Correspondence to Author:**
Peng-dong Wang
School of Earth Science and Engineering, Hebei University of Engineering, Handan 056038, China.

How to cite this article:
Peng-dong Wang. Ge isotopic equilibrium fractionation between Ge-containing ferrihydrite and the aqueous solution. American Journal of Basic and Applied Sciences, 2022; 5:25

eSciPub LLC, Houston, TX USA.
Website: http://escipub.com/

Introduction

In recent years, thanks to the improvement of accurate isotope measuring instruments like multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and the development of precisely analytical methods, non-traditional stable isotopes can be determined for various geological samples, including Si isotopes, Mg isotopes, Fe isotopes, Ge isotopes and so on. In nature, there are five stable Ge isotopes, ^{70}Ge (20.45%), ^{72}Ge (27.41%), ^{73}Ge (7.77%), ^{74}Ge (36.58%), and ^{76}Ge (7.79%) (Rosman and Taylor, 1998). In general, Ge isotopic composition of the sample is expressed as the deviation ‰ from the standard like Aristar, JMC, Spex, Aldrich and NIST SRM3120a, i.e., $\delta^{74}Ge$ (‰) = $[(^{74}Ge/^{70}Ge_{sample})/(^{74}Ge/^{70}Ge_{standard}) - 1] \times 1000$. According to previous studies, the Ge isotopic compositions of river water ($\delta^{74}Ge$ =2.0‰-5.6‰) and seawater ($\delta^{74}Ge$=2.93‰ ~ 3.71‰) (Guillermic et al., 2017; Jotautas Baronas et al., 2017) compared with the continental crust rocks ($\delta^{74}Ge$=0.59±0.18‰) (Escoube et al., 2012; Rouxel et al., 2006) has heavier Ge isotopic compositions. In order to achieve a global Ge isotope balance, there must be a reservoir relatively being enriched in light Ge isotopes in the surface of the earth. Beside organic matter (Li et al., 2009; Qi et al., 2011) and sulfides (Escoube et al., 2012; Li et al., 2009; Meng et al., 2015), Fe oxyhydroxides are another important candidate. There have been two studies on Ge isotopic equilibrium fractionation during adsorption on Fe oxyhydroxide surfaces (Li and Liu, 2010; Pokrovsky et al., 2014). However, previous EXAFS data showed that Ge occurred in the ferrihydrite structure by filling the tetrahedral vacancy and coordinating to four edge-sharing FeO_6 trimers through sharing a common oxygen (≡Ge-O-Fe≡) (Paktunc et al., 2013). The local structure around Ge mimics a Keggin-like motif. Is the Ge isotopic equilibrium fractionation between internal Ge and the solution obviously different from that generated during adsorption on surfaces? It needs further works to resolve this problem.

In this study, we selected ferrihydrite, a ubiquitous Fe oxyhydroxide in the soil and sediment. The first-principles calculation method based on the density functional theory (DFT) was employed to accurately quantify the equilibrium fractionation between internal-Ge-containing ferrihydrite and the aqueous solution.

1. Theory and method

In the present study, molecular clusters were optimized with the hybrid functional B3LYP, as the exchange correlation function, and all electron basis set 6-311G(d), which was used to describe the wave function of the system (Blaudeau et al., 1997; McLean and Chandler, 1980). When the geometric optimization is completed, the harmonic vibrational frequency is analyzed. To determine the absence of imaginary frequency for each set of optimized geometric configurations, it is necessary to ensure that the configuration at least corresponds to the local minima on the potential energy surface. All geometric optimization, electronic energy calculation and harmonic vibrational frequency analyses were completed by Gaussian 09 code (Frisch et al., 2010).

1.1 Calculation of isotope equilibrium fractionation factor

For an ideal system of isotope exchange reactions between the compound and the ideal single-atom gas:

$$AX+X' \rightleftharpoons AX'+X \qquad （1）$$

Which X' denotes an ideal single-atom gas containing heavy isotopes, X represents an ideal single-atom gas containing light isotopes, AX for a compound with a light isotope, AX' for a compound with a heavy isotope.

Bigeleisen and Mayer, (1947) and Urey, (1947) quantitatively established the enrichment extent of heavy isotopes in compounds relative to the ideal single-atom gas, that is, the reduced partition function ratio (RPFR). This parameter is mainly based on the harmonic vibrational frequencies of the compound before and after isotopic substitution, which can be expressed as follows:

$$\mathrm{RPFR}_{AX}=\prod^{3n-6}\frac{u'}{u}\left(\frac{e^{-\frac{u'}{2}}}{e^{-\frac{u}{2}}}\right)\left(\frac{1-e^{-u}}{1-e^{-u'}}\right) \qquad (2)$$

Which u=hcω/kT, h represents the Planck constant; c is the velocity of light; ω denotes the harmonic vibrational frequency (cm^{-1}); k is the Boltzmann constant; T represents the absolute temperature in Kelvin. Specific calculation formula can refer to He et al. (2016) and Liu et al. (2010). If only one isotope is substituted in the compound, the RPFR value is equal to the β factor, which is an isotopic fractionation between a compound and an ideal atomic gas (Richet et al., 1977). The more the RPFR is greater than one, the more heavy isotopes are enriched in the compound.

When the RPFRs of two phases A and B in equilibrium are known, the isotopic fractionation factor can be calculated out by the ratio of their RPFRs (or β factors):

$$\alpha_{A\text{-}B}=\frac{\mathrm{RPFR}_A}{\mathrm{RFFR}_B}=\frac{\beta_A}{\beta_B} \qquad (3)$$

Geochemists usually express the isotope fractionation with Δ, i.e., Δ ≈ 1000lnα. Meanwhile, Δ value can be experimentally determined by the δ difference of two phases in equilibrium ($\Delta_{A\text{-}B}=\delta_A-\delta_B$). This is an important link between theoretical calculation and experimental determination.

Meanwhile, the minimizing root-mean-square error (RMSE) method is used to determine the plateau of RPFR for the Ge-containing species (Ji et al., 2022), calculated as follows:

$$\mathrm{RMSE}=\sqrt{\frac{\sum_1^n (X-Y)^2}{n}} \qquad (4)$$

Which X represents each RPFR value, and Y denotes the expected plateau. The RMSE value changes with the Y value. When the RMSE value reaches a minimum, the corresponding Y value is considered as the plateau of the Ge-containing species.

1.2 Construction of molecular cluster model

In natural water including seawater and river water, Ge mainly exist in the form of $H_4GeO_4\cdot(H_2O)_n$. In this study, we employed the "water-droplet" to simulate H_4GeO_4 aqueous solutions (Liu and Tossell, 2005). When constructing the initial configurations of aqueous H_4GeO_4, we placed single H_4GeO_4 molecules at the center of the molecular cluster, and added six water molecules to cover it. The added water molecules were placed in the bond-forming distance of hydrogen bonds (ca. 1.8 Å - 2.1 Å). We carried out geometric optimization, extracted harmonic vibrational frequencies and calculated RPFR values. We continued to add six water molecules to the optimized configuration to build up the initial configurations of the next group of solutions, and then optimized them. This treatment was repeated until the internal H_4GeO_4 were completely covered by several layers of water molecule and the RPFR values converged to the plateau.

We constructed neutral Ge-containing Ferrihydrite by replacing the ^{IV}Fe in the Keggin ion $[^{IV}FeO_4(^{VI}Fe(OH)_2(H_2O))_{12}]^{7+}$ with Ge and deprotonating, and added water molecules in the outer-sphere (Das, 2018). For the notorious character of Fe-containing systems, we compared the relative electronic energy of Ge-containing ferrihydrite with different spin multiplicity (Table 1), and finally determined the most suitable spin multiplicity S=61.

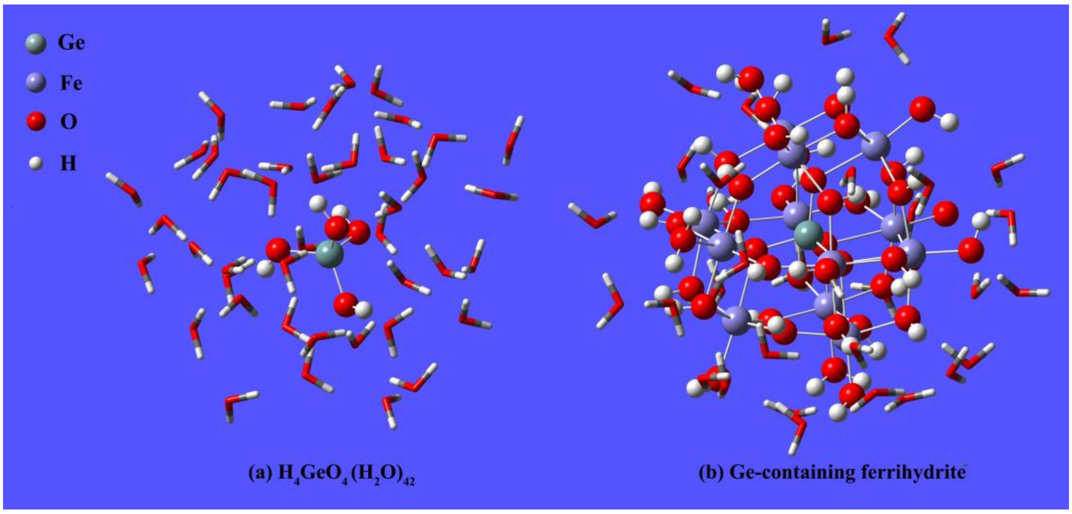
Table 1 The relative electronic energy differences among Ge-containing ferrihydrites with different spin multiplicities.

Spin multiplicity	Relative electronic energy
S=59	21 $KJmol^{-1}$
S=61	0
S=63	398 $KJmol^{-1}$

2. Results and discussion

The optimized geometric configuration was shown in Fig.1. The average Ge-O bond lengths of the optimized H_4GeO_4 aqueous solution and Ge-containing ferrihydrites were 1.77 Å and 1.78 Å, consistent with Li et al. (2009) theoretical calculations (1.76 - 1.78 Å) and Paktunc et al. (2013) experimental results (1.76 Å), respectively. This good agreement ensured the correctness of Ge isotopic equilibrium fractionation factor to some extent.

According to Equation (2), we calculated the RPFR values of H_4GeO_4 aqueous solution at 298.15K. The average of RPFR was selected when identical number of water molecules occurring in the hydrosphere. When the number of water molecules in the hydration layers gradually increases (up to 42 water molecules, Fig.1a), the value of RPFR shows regular changes, fluctuating up and down based on a certain value, which is the plateau value (Fig.2). The minimum root mean square method (Equation (4)) was used to search the exact plateau value. Finally, the plateau value of the RPFR values of H_4GeO_4 aqueous solution was 1.0209.



(a) $H_4GeO_4(H_2O)_{42}$

(b) Ge-containing ferrihydrite

Fig.1 Optimized geometrical structures of H_4GeO_4 aqueous solution and Ge-containing ferrihydrite

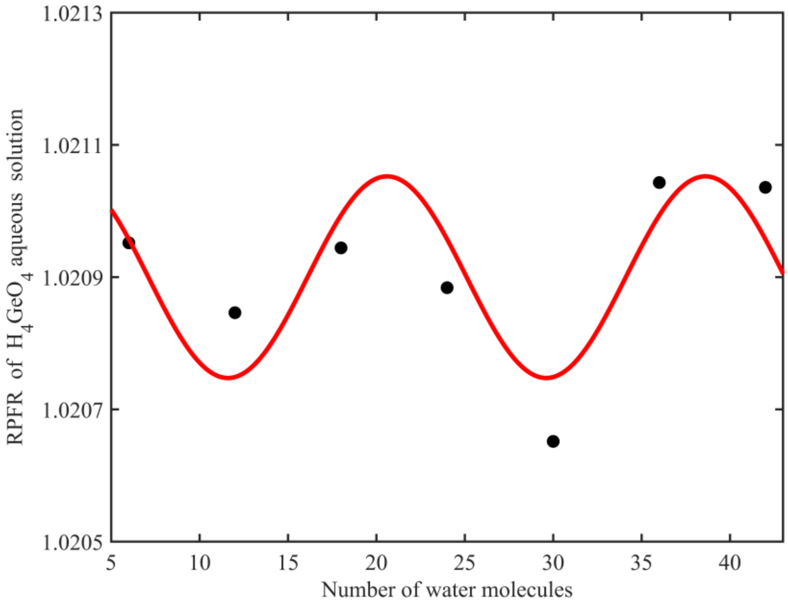


Fig.2 Variations in the RPFR value of H_4GeO_4 aqueous solution with varying numbers of water molecules

Similarly, we also added water molecules to surround the ferrihydrite cluster as its surface solvent. We calculated the Ge isotopic equilibrium fractionation between Ge-containing ferrihydrites and H_4GeO_4 aqueous solution ($\Delta^{74/70}Ge_{ferrihydrite\text{-}aq}$) at 298.15 K. When the number of water molecules in the hydration layers gradually increases (up to 32 water molecules, Fig.1b), the value of $\Delta^{74/70}Ge_{ferrihydrite\text{-}aq}$ shows converged (Fig.3). Finally, we determined the plateau value of $\Delta^{74/70}Ge_{ferrihydrite\text{-}aq}$ as -1.97‰.

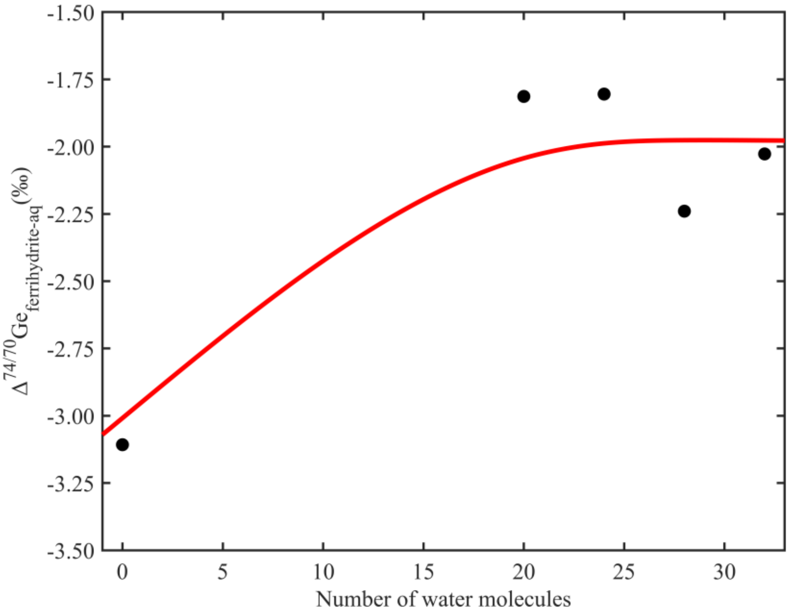


Fig.3 Variations in the $\Delta^{74/70}Ge_{ferrihydrite\text{-}aq}$ with varying numbers of water molecules

Our results show that Ge isotopes significantly fractionate between Ge-containing ferrihydrite and H_4GeO_4 aqueous solution, and light Ge isotopes will be preferentially enriched in ferrihydrite precipitating from the solution. Li and Liu (2010) calculated the Ge isotopic equilibrium fractionation during adsorption onto Fe (III)-oxyhydroxide surfaces as about -1.7‰, consistent with our result (-1.97‰). Fortunately, Ge isotope fractionation experimentally determined for Ge adsorption on goethite (-1.7 ± 0.1‰) also confirmed our calculations (Pokrovsky et al., 2014).

3. Conclusion

In this study, we optimized the geometric configurations of the Ge-containing ferrihydrites and H_4GeO_4 aqueous solution by the first-principles calculation method, and finally at 298.15 K obtained the Ge isotopic equilibrium fractionation factor between Ge-containing ferrihydrites and H_4GeO_4 aqueous solution was -1.97‰，in good agreement with previous theoretical and experimental data.

Acknowledgements

This work was financially supported by the Hebei Natural Sciences Foundation (Nos. D2020402004 and D2021402020), Hebei Education Department Key Program (No. ZD2018086), and State Natural Sciences Foundation (No. 41603011).

References

[1] Bigeleisen J, Mayer M G. 1947. Calculation of Equilibrium Constants for Isotopic Exchange Reactions[J]. The Journal of chemical physics, 15(5): 261-267.

[2] Blaudeau J, Mcgrath M P, Curtiss L A, Radom L. 1997. Extension of Gaussian-2 (G2) theory to molecules containing third-row atoms K and Ca[J]. The Journal of chemical physics, 107(13): 5016-5021.

[3] Das B. 2018. Theoretical Study of Small Iron–Oxyhydroxide Clusters and Formation of Ferrihydrite[J]. The journal of physical chemistry. A, Molecules, spectroscopy, kinetics, environment, & general theory, 122(2): 652-661.

[4] Escoube R, Rouxel O J, Luais B, Ponzevera E, Donard O F X. 2012. An intercomparison study of the germanium isotope composition of geological reference materials[J]. Geostandards and geoanalytical research, 36(2): 149-159.

[5] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA, Peralta JE Jr, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Comperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ. 2010. Gaussian 09, Revision C.01[J].

[6] Guillermic M, Lalonde S V, Hendry K R, Rouxel O J. 2017. The isotope composition of inorganic germanium in seawater and deep sea sponges [J]. Geochimica et cosmochimica acta, 212: 99-118.

[7] He H, Zhang S, Zhu C, Liu Y. 2016. Equilibrium and kinetic Si isotope fractionation factors and their implications for Si isotope distributions in the Earth’s surface environments[J]. Acta geochimica, 35(1): 15-24.

[8] Ji X, Wang Y, Xing L, Liu J, Wang P, Zhang T, Zhao H. 2022. First-principle study of Ba isotopic fractionation during ion exchange processes[J]. Acta geochimica, 41(1): 121-131.

[9] Jotautas Baronas J, Hammond D E, Mcmanus J, Wheat C G, Siebert C. 2017. A global Ge isotope budget[J]. Geochimica et cosmochimica acta,

203: 265-283.

[10] Li X F, Liu Y. 2010. First principles study of Ge isotope fractionation during adsorption onto Fe(III)-oxyhydroxide surfaces[J]. Chemical geology, 278(1-2): 15-22.

[11] Li X, Zhao H, Tang M, Liu Y. 2009. Theoretical prediction for several important equilibrium Ge isotope fractionation factors and geological implications[J]. Earth and planetary science letters, 287(1-2): 1-11.

[12] Liu Q, John A T, Liu Y. 2010. 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, 74(24): 6965-6983.

[13] Liu Y, Tossell J A. 2005. Ab initio molecular orbital calculations for boron isotope fractionations on boric acids and borates[J]. Geochimica et cosmochimica acta, 69(16): 3995-4006.

[14] Mclean A D, Chandler G S. 1980. Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z =11–18[J]. The Journal of chemical physics, 72(10): 5639-5648.

[15] Meng Y, Qi H, Hu R, Wang R, Zhou M. 2015. Determination of germanium isotopic compositions of sulfides by hydride generation MC-ICP-MS and its application to the Pb-Zn deposits in SW China[J]. Ore geology reviews, 65: 1095-1109.

[16] Paktunc D, Manceau A, Dutrizac J, Argonne National Lab. Anl A I U S. 2013. Incorporation of Ge in ferrihydrite; implications for the structure of ferrihydrite[J]. The American mineralogist, 98(5-6): 848-858.

[17] Pokrovsky O S, Galy A, Schott J, Pokrovski G S, Mantoura S. 2014. Germanium isotope fractionation during Ge adsorption on goethite and its coprecipitation with Fe oxy(hydr)oxides[J]. Geochimica et cosmochimica acta, 131: 138-149.

[18] Qi H, O R, Hu R, Bi X, Wen H. 2011. Germanium isotopic systematics in Ge-rich coal from the Lincang Ge deposit, Yunnan, southwestern China[J]. Chemical geology, 286(3-4): 252-265.

[19] Richet P, Bottinga Y, Javoy M. 1977. A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules[J]. Annual review of earth and planetary sciences, 5(1): 65-110.

[20] Rosman K J R, Taylor P D P. 1998. Isotopic Compositions of the Elements 1997[J]. Journal of physical and chemical reference data, 27(6): 1275-1287.

[21] Rouxel O, Galy A, Elderfield H. 2006. Germanium isotopic variations in igneous rocks and marine sediments[J]. Geochimica et cosmochimica acta, 70(13): 3387-3400.

[22] Urey H C. 1947. The thermodynamic properties of isotopic substances[J]. Journal of the Chemical Society: 562-581.