

# Equilibrium sulfur isotope fractionations of several important sulfides

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The volume variable cluster model method, which is an improvement proposed by Rustad and coworkers, has been successfully used to calculate equilibrium isotope fractionations between solids and solutions. The biggest difference between these two cluster model methods is that the fixed layer of atoms in the method of Rustad *et al.* has been removed and the whole cluster is freely optimized under the “VVCM” (the volume variable cluster model method) treatment. In this paper, several sulfides have been chosen whose sulfur isotope fractionations have been theoretically studied by previous researchers but with disagreements on calculating sulfur isotope fractionations.  $\text{HS}^-_{(\text{aq})}$  and  $\text{H}_2\text{S}_{(\text{aq})}$  solutions are used to model sulfur-bearing aqueous solutions under different conditions. The calculated results of the first-principles DFT method are quite different from those based on Mössbauer data. The VVCM-based method is completely different from both of the above methods and can therefore provide an independent evaluation of their results. The results in this article show that the  $\beta$ -factors of sulfides decrease in the order of pyrite > sphalerite > galena and that the sulfur isotope fractionation magnitudes are in good agreement with previous results.

Keywords: equilibrium sulfur isotope fractionation, ab initio calculation, sphalerite, galena, pyrite

## INTRODUCTION

Sulfur is a non-metallic and abundant element in the Earth and its crust. It is a multivalent element with four common valence states:  $-2$ ,  $0$ ,  $+4$  and  $+6$ . The chemical symbol for elemental sulfur is S, its atomic number is 16, and it is located in the third cycle and sixth group (VIA) of the periodic table of elements. In nature, sulfur mainly exists as compounds such as sulfides (e.g., sphalerite, galena and pyrite) and sulfates (e.g., gypsum). Elementary substances of sulfur can also be found in reducing environments such as some volcanic areas. In addition, sulfur is an essential element for life because it is an important component of proteins in organisms, and it is both important and significant for human life activities.

Sulfur has four different stable isotopes,  $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$  and  $^{36}\text{S}$ , with relative abundances of 95.04, 0.75, 4.20 and 0.01%, respectively (de Laeter *et al.*, 2003). A few decades ago, sulfur geochemistry became a very important subdiscipline of the geological sciences. The earliest studies on sulfur isotopes date back to the 1940s (Thode *et al.*, 1949; MacNamara and Thode, 1950; Szabo *et al.*, 1950; Sakai, 1957; Thode *et al.*, 1961). For a long time,

sulfur isotope analyses have been applied to ore deposits; the pioneers of this subject area are Kulp *et al.* (1956) and Jensen (1957, 1959), among others. At present, sulfur isotopes are used in the fields of geology (e.g., Shanks *et al.*, 1981), biology (e.g., Rees, 1973; Habicht and Canfield, 1997; Habicht *et al.*, 1998; Bolliger *et al.*, 2001; Brüchert *et al.*, 2001; Detmers *et al.*, 2001) and environmental science (e.g., Harris *et al.*, 2013), etc. Notably, research on the mass-independent fractionation of sulfur is currently the most active topic in the field of sulfur isotope geochemistry (Farquhar *et al.*, 2000, 2001, 2013; Savarino *et al.*, 2003; Subrata *et al.*, 2013).

It is well known that equilibrium isotope fractionation can be used to estimate the formation temperature of minerals in geological systems (Urey and Greiff, 1935; Urey, 1947). Isotope geochemistry mainly focuses on the change in the isotope ratio between different species rather than on their absolute abundances. The general rule for isotope fractionation is that heavy isotopes tend to form more stable chemical bonds; for example,  $\text{M}^{34}\text{S}$  is more stable than  $\text{M}^{32}\text{S}$  (M stands for metal cations). When considering kinetic isotope effects, molecules with different isotopes have different reaction rates (O’Neil, 1986). In the case of sulfur,  $^{34}\text{S}/^{32}\text{S}$  is the key point of interest. In most cases, isotope fractionation is relatively small, and most of the time, the  $\delta$  notation is used to express isotope fractionation. In this article, only the ratio of  $^{34}\text{S}/^{32}\text{S}$  is

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given attention because  $^{34}\text{S}$  and  $^{32}\text{S}$  are the most abundant sulfur isotopes, which makes them convenient to analyse in experiments. The isotope fractionations of different sulfur isotopes follow mass-dependent fractionation, i.e., the relative fractionation values of  $^{33}\text{S}/^{32}\text{S}$  and  $^{36}\text{S}/^{32}\text{S}$  can be obtained through the mass-dependent fractionation law (Urey, 1947; MacNamara and Thode, 1950; Hulston and Thode, 1965).

Sulfur is a key factor affecting the formation of sulfide minerals and can indicate the formation processes and origins of these minerals. Because of different isotopic compositions of sulfide minerals and sulfates (e.g., sulfate minerals and sulfate aqueous solutions), sulfur isotope fractionation could commonly exist between these S-bearing species. Because sulfur is a multivalent element, both the temperature difference and the redox reactions between different S-bearing species can bring about sulfur isotope fractionation. Redox reactions can occur in different geological environments, such as igneous systems, hydrothermal systems and sedimentary diagenesis.

The isotope fractionation factor is a very important parameter when conducting research in the fields of geology, biology, agricultural science, etc. There are three methods to obtain isotope fractionation factors, i.e., experimental methods, theoretical calculation methods and direct acquisition through measuring the isotope ratio of natural samples (Seal *et al.*, 2000). Much research has been devoted to obtaining sulfur isotope fractionation through experimental measurements (Grootenboer and Schwarcz, 1969; Kajiwarra *et al.*, 1969; Rye and Czamanske, 1969; Schiller *et al.*, 1970; Kajiwarra and Krouse, 1971; Salomons, 1971; Kiyosu, 1973; Czamanske and Rye, 1974; Smith *et al.*, 1977; Hubberten, 1980). In addition, theoretical calculations about the sulfur isotope fractionation of sulfides have been published (Sakai, 1968; Groves *et al.*, 1970; Elcombe and Hulston, 1975; Li and Liu, 2006; Otake *et al.*, 2008; Blanchard *et al.*, 2009; Polyakov and Soultanov, 2011; Liu *et al.*, 2014, 2015, 2018; Polyakov *et al.*, 2019).

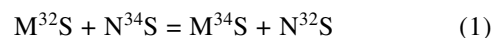
By definition, the isotope fractionation factor is equal to the ratio of  $\beta$ -factors of two different substances through the theoretical calculation method. At present, some groups have investigated the  $\beta$ -factors of S-bearing minerals such as sphalerite, galena and pyrite worldwide. Calculating the Fe isotope fractionation factor according to Mössbauer data is related to the accuracy of the experimental spectrum. The equilibrium isotope fractionation factor can be calculated through the reduced partition function ratio (RPFR), e.g., the  $\beta$ -factor. The  $\beta$ -factor can not be measured directly by experimental methods; however, it can be calculated through various theoretical calculation methods. Among all these theoretical methods, Polyakov's method is based on the elements that have Mössbauer activity. After the papers by Blanchard

*et al.* and Polyakov and Soultanov were published, Syverson *et al.* (2013) provided an exchange of Fe under hydrothermal conditions. The result of Polyakov *et al.* (2013) is consistent with experimental measurements conducted by Syverson *et al.* Therefore, Polyakov used an indirect method that calculated the S isotope fractionation between pyrite and other S-bearing minerals, such as sphalerite and galena, to obtain the Fe isotope fractionation factor of pyrite ( $\beta$ -factor). Polyakov and Soultanov (2011) said that the result of the Fe  $\beta$ -factor of pyrite they acquired was not accurate. Nevertheless, they suggested that the data obtained by Blanchard *et al.* (2009), who used the DFT method, underestimated the real value of the Fe  $\beta$ -factor of pyrite. Blanchard *et al.* Suggested that the difference between these two  $\beta$ -factors stemmed from the input data (second-order Doppler shift (SOD shift)) of Polyakov *et al.* In detail, Blanchard *et al.* used the first-principles method based on density functional theory, while Polyakov and Soultanov obtained the  $\beta$ -factors through the factor (heat capacity) obtained by Ogawa (1976) and factors obtained from the Mössbauer SOD shift by Nishihara and Ogawa (1979). They carried out investigations on the  $\beta$ -factors of S-bearing minerals because of the relationship between the  $\beta$ -factors of sulfur (S) and iron (Fe). Polyakov *et al.* considered that their theoretical results of isotope fractionation factors were in good agreement with the experimental values obtained by Smith *et al.* (1977), Kajiwarra *et al.* (1969) and Kajiwarra and Krouse (1971), while the difference between the theoretical values of Blanchard *et al.* and these aforementioned experimental values was significant. Fortunately, the difference in  $\beta$ -factors for pyrite provided by Blanchard *et al.* (2009) and Polyakov and Soultanov (2011) has been resolved by Polyakov's team (Polyakov *et al.*, 2019). This study uses the theoretical calculation method of the cluster model to re-calculate the  $\beta$ -factors of sphalerite, galena and pyrite as well as S-bearing solutions such as  $\text{HS}^-$  solution and  $\text{H}_2\text{S}$  solution.

## THEORY AND METHODS

*Equilibrium isotope fractionation: the Bigeleisen-Mayer equation or Urey model*

The Bigeleisen-Mayer equation, or the Urey model (Bigeleisen and Mayer, 1947; Urey, 1947), is the cornerstone of theoretical and computational stable isotope geochemistry. Through this calculation, the equilibrium isotope exchange constant K can be obtained. The sulfur isotope exchange reaction between different sulfides, which in the case of only one atom exchanged, is used; for example



where MS and NS stand for two kinds of sulfides.  $M^{34}S$  and  $N^{34}S$  are molecules with heavier sulfur isotopes relative to  $M^{32}S$  and  $N^{32}S$ , respectively. M and N are metal cations, and S indicates sulfur. The reaction equilibrium constant K equals the ratio of the concentrations of the products to the reactants, i.e.,

$$K = \frac{[M^{34}S]}{[M^{32}S]} \bigg/ \frac{[N^{34}S]}{[N^{32}S]} \quad (2)$$

where “[ ]” are the concentrations of different substances in the isotope exchange reaction.

Thermodynamically, the reaction equilibrium constant K can also be expressed by the partition functions (Q) of all substances involved in the reaction.

$$K = \frac{Q_{M^{34}S}}{Q_{M^{32}S}} \bigg/ \frac{Q_{N^{34}S}}{Q_{N^{32}S}} \quad (3)$$

$Q_{M^{34}S}$ ,  $Q_{M^{32}S}$ ,  $Q_{N^{34}S}$  and  $Q_{N^{32}S}$  stand for the partition functions of  $M^{34}S$ ,  $M^{32}S$ ,  $N^{34}S$  and  $N^{32}S$ , respectively.

The Urey model, or Bigeleisen-Mayer equation, suggests that the reaction constant is equivalent to the ratio of the reduced partition function ratio (RPFR, also called the  $\beta$ -factor) of the two substances or of two different phases when there is only one atom exchanged in the isotope exchange reaction.

$$K = \frac{\text{RPFR}(\text{MS})}{\text{RPFR}(\text{NS})} = \frac{\beta(\text{MS})}{\beta(\text{NS})}. \quad (4)$$

According to the definition by Bigeleisen and Mayer (1947), the expression of the RPFR can be stated as follows:

$$\text{RPFR} = \beta = \left( \frac{s^*}{s} \right) \prod_i^{3n-6} \frac{u_i \exp(-u_i/2)}{u_i^* \exp(-u_i^*/2)} \frac{1 - \exp(-u_i^*)}{1 - \exp(-u_i)} \quad (5)$$

where “s” is the symmetry number of the molecule or cluster. The asterisk represents molecules with heavier isotopes. Parameter  $u_i$  can be acquired from the harmonic vibrational frequency  $\nu_i$

$$u_i = \frac{h\nu_i}{k_b T} \quad (6)$$

where h,  $k_b$  and T are the Planck constant, Boltzmann constant and temperature in Kelvin, respectively.

If there are n atoms exchanged in an isotope exchange reaction, then the RPFR =  $\beta^n$ . However, in the field of geochemistry, the isotope fractionation factor  $\alpha$  is always used instead of the equilibrium constant K. The relationship between  $\alpha$  and K is  $\alpha = K^{1/n}$ , where n is the number of atoms exchanged during the isotope exchange reaction. If there is only one isotope atom exchanged during the reaction, then

$$\alpha = K. \quad (7)$$

Since  $\alpha$  is very close to 1 in all cases considered in this study, the isotope shift between substances MS and NS can be written as follows:

$$\Delta_{\text{MS-NS}}(\text{‰}) \approx 10^3 \ln \alpha_{\text{MS-NS}}. \quad (8)$$

In Eq. (8), the capital delta “ $\Delta$ ” represents the difference in isotopic compositions of substances MS and NS:  $\Delta_{\text{MS-NS}}(\text{‰}) \approx \delta_{(\text{MS})} - \delta_{(\text{NS})}$ .

Through this model, the equilibrium isotope fractionation factor can be obtained through the harmonic vibrational frequencies of two substances or two different phases of one substance. The magnitude of isotope fractionation is inversely proportional to the temperature. In extreme cases, such as when the temperature is high enough,  $\ln \alpha$  and  $\ln \beta$  are proportional to the square of the inverse temperature.

#### Theory and calculation method

The Urey model, or Bigeleisen-Mayer equation, was established in 1947 (Bigeleisen and Mayer, 1947; Urey, 1947). Since then, an increasing number of researchers have focused their interest on the calculation method of equilibrium isotope fractionation factors (e.g., Richet *et al.*, 1977; Bigeleisen, 1996, 1998; Liu *et al.*, 2010). Although early studies of theoretical calculations of equilibrium isotope fractionation factors were based on experimental spectrum data, and such calculations were very tedious due to a lack of modern computing facilities, these calculations still obtained the direction, magnitude and temperature dependence of isotope fractionation factors well. However, the incompleteness or inaccuracy of spectrum data limits the development of theoretical and computational geochemistry. In the past several years, with the tremendous development in computer technology, it has been possible to calculate the simple harmonic vibrational frequencies of macromolecules, molecule clusters and even condensed phases. Theoretical and computational geochemistry has again become one of the most characteristic and active subdisciplines of geochemistry. At present, the ab initio quantum chemistry method is used to calculate the simple harmonic vibrational frequencies of different molecules (Hehre *et al.*, 1986). This

method has been widely used to calculate isotope fractionation factors between different terrestrial samples (Oi, 2000; Oi and Yanase, 2001; Schauble *et al.*, 2003, 2006; Jarzecki *et al.*, 2004; Schauble, 2004, 2007; Anbar *et al.*, 2005; Liu and Tossell, 2005; Rustad and Bylaska, 2007; Seo *et al.*, 2007; Otake *et al.*, 2008; Rustad *et al.*, 2008; Rustad and Zarzycki, 2008; Fujii *et al.*, 2009, 2010; Li *et al.*, 2009; Li and Liu, 2010; Black *et al.*, 2011; Li and Liu, 2011). Theoretical calculation results can explain the mechanics in the experimental results. In this study, the isotope fractionation of sulfur between different solutions and S-bearing minerals was investigated. The cluster model and water-droplet method were used to model the condensed phases of different minerals and the solvation effect in aqueous solutions, respectively.

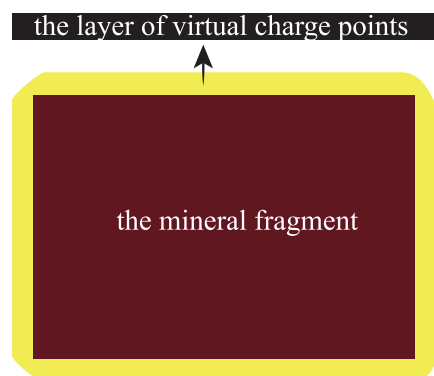


Fig. 1. Sketch map of the volume variable cluster model method (VVCM). Brown and yellow represent the mineral fragments (structures) and the layer of virtual charge points, respectively. For virtual charge points, the easiest way is used, i.e., hydrogen atoms are added to mineral fragments. This is done to hold the outer layer atoms in place. The distances between virtual charges and the outer layer atoms of fragments can be changed; that is, the layer of virtual charge points is flexible. This allows the whole mineral fragment to be freely optimized.

Gaussian03 software was used throughout the research (Frisch *et al.*, 2003).

**Cluster method** In this study, all the S-bearing minerals were simulated in the cluster model, and the process of simulating solid phases is a great improvement to the method of Rustad *et al.* (2008). In this method, the fixed layer of atoms in Rustad's method was removed, and the whole mineral fragment was not only freely optimized but the layer of virtual charge points was also flexible. This layer was adjustable, and the whole fragment was freely optimized to an energy minimum point, i.e., the most stable geometry. In addition, the same theoretical level should be used for two phases to avoid errors caused by different theoretical levels. This method was named the "volume variable cluster model method, or VVCM" (Fig. 1) (He and Liu, 2015; He *et al.*, 2016; Gao *et al.*, 2018; Zhang and Liu, 2018).

When establishing cluster models, there are several rules that must be followed to make the models reasonable. First, the atoms of interest (such as sulfur) were placed in the centre of different unit cells. Second, the most important rule was that the outer layers of the clusters must be surrounded by atoms with negative charges. After the establishment of cluster models, virtual charges (positive charges) needed to be added to the outer shells of the clusters to neutralize the negative charges. The lengths between the outer shell atoms and virtual charges were always regarded as an experiential problem. A series of clusters with different lengths between the outer layer atoms and virtual charges were optimized for the purpose of acquiring the geometry with minimum energy, i.e., the most stable structure. The basis set of B3LYP/6-311G(d) was used throughout the study when optimizing the solid phases. The clusters contain 44 atoms (38 S atoms and 6 Fe atoms), 83 atoms (28 Zn atoms and 55 S atoms) and 25 atoms (6 Pb atoms and 19 S atoms) for pyrite, sphalerite and galena, respectively. The optimized geometry information and structures of sphalerite, galena

Table 1. Optimized geometry information (bond lengths and bond angles) of S-bearing minerals (pyrite, sphalerite and galena) compared with those from previous studies

Mineral	Bond length (Å)			Bond angle (°)		
	Atoms	Previous study	This study	Atoms	Previous study	This study
Pyrite <sup>a</sup>	Fe-S	2.23–2.30	2.31	S-Fe-S	85–95	93.421
	S-S	2.14–2.17	2.11	Fe-S-Fe	114–117	115.26
				Fe-S-S	101–103	103.45
Sphalerite <sup>b</sup>	Zn-S	2.342	2.347	Zn-S-Zn	109.47	109.58
				S-Zn-S	109.47	109.49
Galena <sup>c</sup>	Pb-S	2.962	2.937	Pb-S-Pb	90	89.89
				S-Pb-S	90	89.57

<sup>a</sup>Bayliss (1977); <sup>b</sup>Skinner (1961); <sup>c</sup>Noda *et al.* (1987).

and pyrite with sulfur atoms in the centre are shown in Table 1 and Fig. 2.

This calculation method is a kind of cluster method. Solid minerals were treated as large clusters, and the whole fragment structure optimization and frequency calculation were performed at a unified theoretical level by Gaussian software. Molecule-like clusters were adopted to represent the sulfide minerals in this paper. This method has been used for a long time to study solid minerals (Gibbs, 1982). Actually, isotopic effects are a kind of “local” property of solid minerals and can decay quickly from 2 or 3 bonds away. In other words, the isotopic effect is mostly affected by the next nearest neighbour atoms that surround the atoms of interest (i.e., the NNN rule) (Liu and Tossell, 2005). With the treatment of the “VVCM” method, sulfide minerals are used as small molecule-like clusters that can be optimized and calculated frequencies at a higher-level theoretical basis set. In some exceptional cases, such as heavy elements having anharmonic effects, minerals with H-bonding and weak interactions can be treated by the VVCM. If the position of the virtual charge is fixed, the result of the calculation is inaccurate. In this method, the distance between the outermost atoms and the virtual charge points can be adjusted. The result of

the calculation shows that the position of the virtual charge points can affect the calculation value of RPFs. The VVCM method can be used to solve systems in which heavy elements have anharmonic effects and minerals with H-bonding and weak interactions, and the method is proven to be efficient by computational simulation (Gao *et al.*, 2018).

However, the method used by Blanchard *et al.* is a kind of periodic structure method with PWSCF code. This is the difference between the VVCM and the method of Blanchard *et al.* Therefore, it is difficult to compare lattice parameters and vibrational frequencies between this study and previous results. To check the accuracy of the calculation method, some small S-bearing molecules’ frequencies are calculated and compared to frequencies in previous studies. A comparison of the vibrational frequencies of some gaseous sulfur ( $^{32}\text{S}$ ) molecules calculated in this study using the ab initio method with the experimental value is shown in Table 2.

*Models of  $\text{HS}^-$  and  $\text{H}_2\text{S}$  in aqueous solution: the water-droplet method* In this article, the “water-droplet” method was used to model the solvation effect in aqueous solutions. Under reducing conditions,  $\text{HS}^-$  in solution is the dominant species of S-bearing solutions in fluids and so-

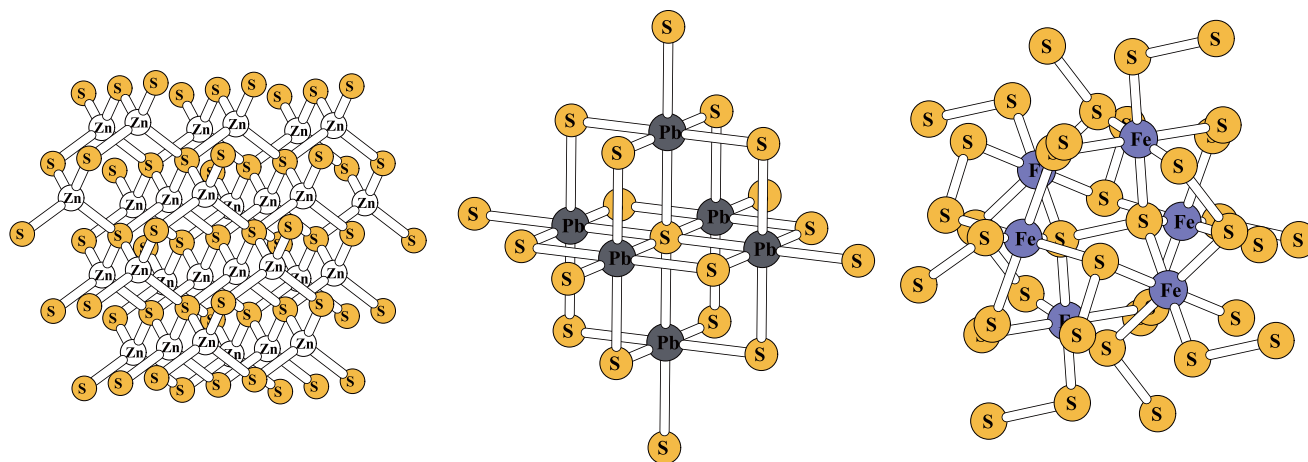


Fig. 2. Crystal structures of sphalerite, galena and pyrite with S atoms in the centre. The central sulfur atoms are quadridentate, hexa-coordinate and quadridentate for sphalerite, galena and pyrite, respectively.

Table 2. Comparison of vibrational frequencies of some small S-bearing molecules between this study and previous studies. All the frequencies were calculated at the basis set of B3LYP/6-31G(d) for this study and the work of Otake *et al.* (2008)

Method	Frequencies ( $\text{cm}^{-1}$ )													
	$\text{H}_2\text{S}$		$\text{S}_2$	$\text{SO}_2$			$\text{SO}_3$			$\text{CS}_2$				
Experimental	1183 <sup>a</sup>	2615 <sup>a</sup>	2626 <sup>a</sup>	720 <sup>b</sup>	518 <sup>a</sup>	1151 <sup>a</sup>	1362 <sup>a</sup>	498 <sup>a</sup>	530 <sup>a</sup>	1065 <sup>a</sup>	1391 <sup>a</sup>	397 <sup>a</sup>	658 <sup>a</sup>	1535 <sup>a</sup>
Otake <i>et al.</i> (2008)	1202	2588	2608	670	483	1096	1285	437	478	983	1299	389	648	1497
This study	<b>1246</b>	<b>2606</b>	<b>2624</b>	<b>675</b>	<b>509</b>	<b>1139</b>	<b>1325</b>	<b>461</b>	<b>498</b>	<b>1020</b>	<b>1343</b>	<b>392</b>	<b>673</b>	<b>1553</b>

<sup>a</sup>Shimanouchi (1972); <sup>b</sup>Huber and Herzberg (1979).

lutions. The central  $\text{HS}^-$  anion is surrounded by many water molecules. Experimental results have shown that sulfur isotope exchange between S-bearing minerals (such as sphalerite, galena and pyrite) and  $\text{HS}^-$  solutions is very fast (Northrop and Clayton, 1966; Kiyosu, 1973). In this study, an  $\text{HS}^-$  solution was used to simulate S-bearing solutions under reducing conditions. To obtain the optimized structure of  $\text{HS}^-$  in diluted aqueous solutions, first, six water molecules were placed surrounding the  $\text{HS}^-$  anion. These six water molecules were treated as the inner shell waters of this complex. Then, the Gaussian03 software package was used to optimize this structure. When the optimized structure was obtained, another six water molecules were placed outside the cluster and

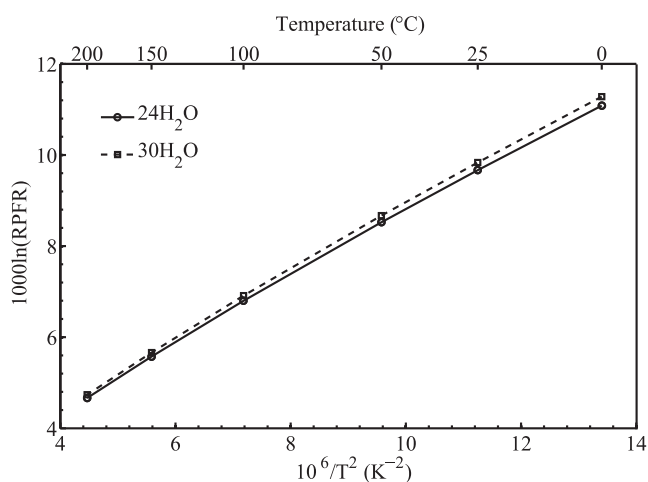


Fig. 3.  $\beta$ -factors (RPFs) of  $\text{HS}^-$  water-droplets with different waters as a function of temperature.

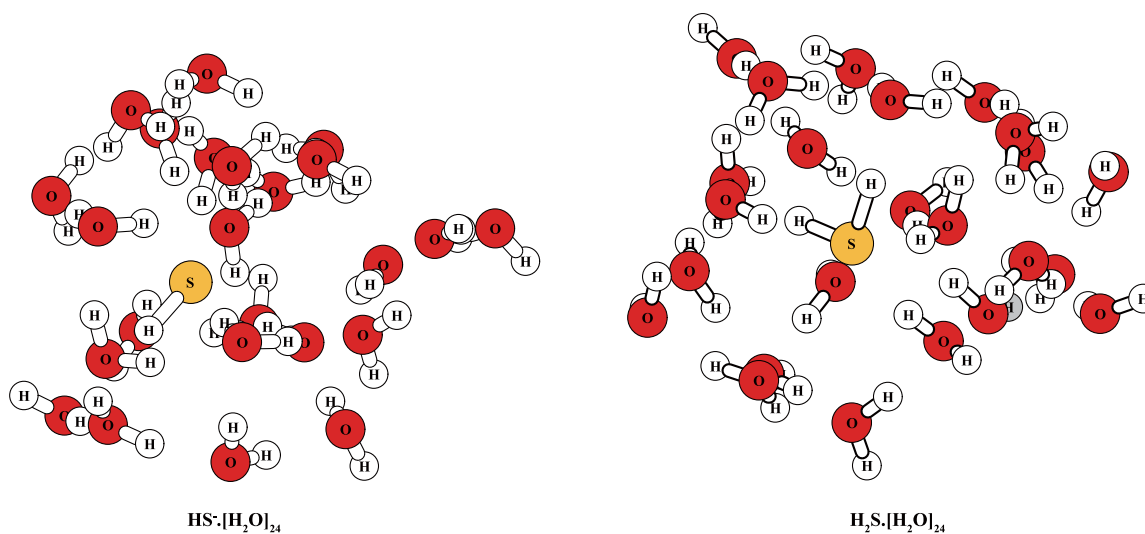


Fig. 4. Optimized structures of  $\text{HS}^- \cdot [\text{H}_2\text{O}]_{24}$  and  $\text{H}_2\text{S} \cdot [\text{H}_2\text{O}]_{24}$  water-droplets.

optimized at the same basis set. This process was repeated until the most stable structure of  $\text{HS}^- \cdot [\text{H}_2\text{O}]_{24}$  was acquired, and then the harmonic vibrational frequencies of the complex were calculated. This is because when exceeding  $24\text{H}_2\text{O}$  to  $\text{HS}^-$ , the magnitude of the  $\beta$ -factors converges to a fixed value. The variation in the trend of  $\beta$ -factors with different waters is shown in Fig. 3. When the number of waters is equal to 24 and 30, the clusters have the same RPF value. Therefore, the structure of  $\text{HS}^- \cdot 24\text{H}_2\text{O}$  may represent S-bearing solutions. Note that the whole process of optimizing geometries and calculating frequencies must be under the same theoretical basis set. The basis set of B3LYP/6-311G(d) was utilized throughout the study to optimize geometries and calculate frequencies of water-droplets. Much time was spent optimizing the geometry and calculating frequencies. From experience, it was unreasonable to first pre-optimize the geometry at a lower basis set and then re-optimized it at a higher basis set to save time. This could cause an inaccurate local structure when using a lower basis set to optimize structures, and this difference could not be eliminated even though re-optimized at a higher theoretical level. If the structure is optimized in this manner, an unreasonable result might be obtained. Under hydrothermal conditions,  $\text{H}_2\text{S}_{(\text{aq})}$  is also an important species. S isotope fractionation between pyrite and  $\text{H}_2\text{S}_{(\text{aq})}$  under hydrothermal conditions has been obtained by experimental study (Syverson *et al.*, 2015). The experimental result shows that the equilibrium fractionation factor between  $\text{FeS}_2$  and  $\text{H}_2\text{S}_{(\text{aq})}$  at  $350^{\circ}\text{C}$  is  $-1.9\%$ . Therefore, the  $\text{H}_2\text{S}$  solution is calculated in the same way. The optimized structure of  $\text{HS}^- \cdot [\text{H}_2\text{O}]_{24}$  and  $\text{H}_2\text{S} \cdot [\text{H}_2\text{O}]_{24}$  water droplets are shown in Fig. 4. Table 3 and Fig. 5 show a comparison between the calculation results of Otake *et al.*, other groups, and

this study. The  $\text{HS}^-_{(\text{aq})}$  and  $\text{H}_2\text{S}_{(\text{aq})}$  results of this study are in great agreement with the results of Eldridge *et al.* (2016) but are different from the results of Otake *et al.* (2008) and Czarnacki and Halas (2012). The  $\beta$  factors calculated in this study are much larger than those calculated in these two previous investigations. Although the equilibrium fractionation factor result between  $\text{FeS}_2$  and  $\text{H}_2\text{S}_{(\text{aq})}$  at  $350^\circ\text{C}$  in this study could not reach  $-1.9\%$ , it was better than previous results. Therefore, the difference between the experimental results and previous theoretical works may be caused by the inaccurate RPFs used for  $\text{H}_2\text{S}_{(\text{aq})}$ .

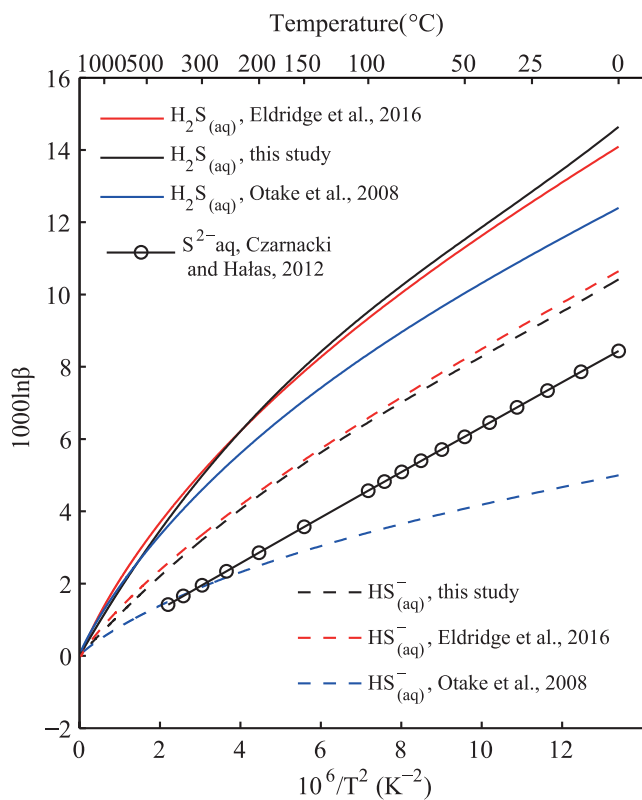


Fig. 5.  $\beta$ -factors of  $\text{HS}^-_{(\text{aq})}$  and  $\text{H}_2\text{S}_{(\text{aq})}$  solutions as a function of temperature.

The calculation results of Otake *et al.* (2008) are based on Table 3 in their article. Their calculations show little difference in isotope fractionation values between the gas and liquid phases. For  $\text{HS}^-$ , the calculation result in this study is almost identical to theirs. However, for  $\text{HS}^-_{(\text{aq})}$ , the difference between these two calculations is quite large. The calculation methods for acquiring the isotope fractionation factor of aqueous species are different. This article uses the “water-droplet” method, while Otake *et al.* used the IEF-PCM model. This may be the source of the difference between these two differing results.

## RESULTS AND DISCUSSION

*The isotope fractionation factor of sulfur between sphalerite and galena*

In experiments, the sulfur isotope fractionation between sulfides (such as  $\text{ZnS}$  and  $\text{PbS}$ ) and the  $\text{HS}^-$  solution can reach an isotope exchange equilibrium state rapidly; however, the isotope exchange between  $\text{ZnS}$  (sphalerite) and  $\text{PbS}$  (galena) is very slow (Kiyosu, 1973). Therefore, researchers always use the isotope exchange reaction between sulfides and the  $\text{HS}^-$  solution to obtain the S isotope fractionation of the sphalerite-galena pair. In this manner, the isotope fractionation factor between these two minerals can be obtained faster. In this theoretical study, the  $\text{HS}^- \cdot 24\text{H}_2\text{O}$  cluster was used to simulate the aqueous solution and calculate the isotope fractionation factor between  $\text{ZnS}$  (or  $\text{PbS}$ ) and  $\text{HS}^-$  solution. The calculated results of fractionation factors as a function of temperature between different S-bearing substances are shown in Fig. 5. This study’s results are in agreement with experimental values (Kajiwara *et al.*, 1969; Kiyosu, 1973; Czamanske and Rye, 1974; Smith, 1977) and values in previous studies (Li and Liu, 2006; Blanchard *et al.*, 2009) at high temperatures ( $>200^\circ\text{C}$ ). However, at low temperatures ( $<170^\circ\text{C}$ ), the difference between the result of this study and the experimental result of Kajiwara *et al.* (1969) is significant. This may result from the experiment not reaching full equilibrium at low temperatures. The result of the isotope fractionation factor of the sphalerite-galena pair in this study is also

Table 3. Comparison of data for  $\text{HS}^-$  and aqueous solutions in the form of  $\beta$  between the calculation results of Otake *et al.* and this work

	Temperature ( $^\circ\text{C}$ )						
	0	25	50	100	150	200	300
$\beta$							
$\text{HS}^-$ (This study)	1.0050	1.0046	1.0041	1.0035	1.0030	1.0025	1.0020
$\text{HS}^-$ (Otake <i>et al.</i> , 2008)	1.0049	1.0044	1.0040	1.0034	1.0029	1.0025	1.0019
$\text{HS}^-_{(\text{aq})}$ (This study)	1.0105	1.0091	1.0080	1.0065	1.0053	1.0044	1.0033
$\text{HS}^-_{(\text{aq})}$ (Otake <i>et al.</i> , 2008)	1.0050	1.0045	1.0041	1.0034	1.0029	1.0025	1.0019

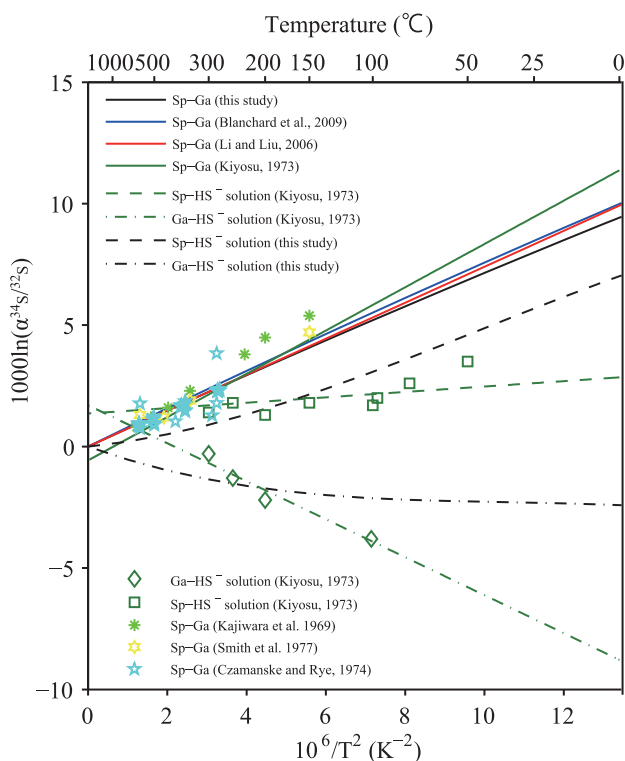


Fig. 6. Isotope fractionation factors of sphalerite-galena, sphalerite- $\text{HS}^-$  solution and galena- $\text{HS}^-$  solution as a function of temperature with the basis set B3LYP/6-311G(d). Sp and Ga stand for sphalerite and galena. The diamond and square are experimental results obtained by Kiyosu (1973) for galena- $\text{HS}^-$  solution and sphalerite- $\text{HS}^-$  solution, respectively. The asterisk, hexagon and pentagon are fractionation factors of sphalerite-galena obtained by Kajiwara *et al.* (1969), Smith *et al.* (1977) and Czamanske and Rye (1974), respectively.

slightly different from theoretical calculations of Blanchard *et al.* and Li and Liu (the solid blue and red lines in Fig. 6, respectively). These small differences may arise from methodological differences. The experimental value of isotope fractionation for sphalerite-galena is also shown in Fig. 6.

#### RPFs of sulfur for sphalerite, galena and pyrite

The isotope fractionation factors between two different compounds (denoted as A and B) can be obtained through both theoretical and experimental approaches. RPF, which is always expressed as the  $\beta$ -factor, can be determined by theoretical methods. From previous studies, we know that there is controversy about the magnitude of sulfur  $\beta$ -factors for different minerals, such as sphalerite, galena and pyrite (Polyakov *et al.*, 2007, 2019; Blanchard *et al.*, 2009, 2012; Polyakov and Soultanov, 2011, 2012).

The  $\beta$ -factors of different sulfides (sphalerite, galena

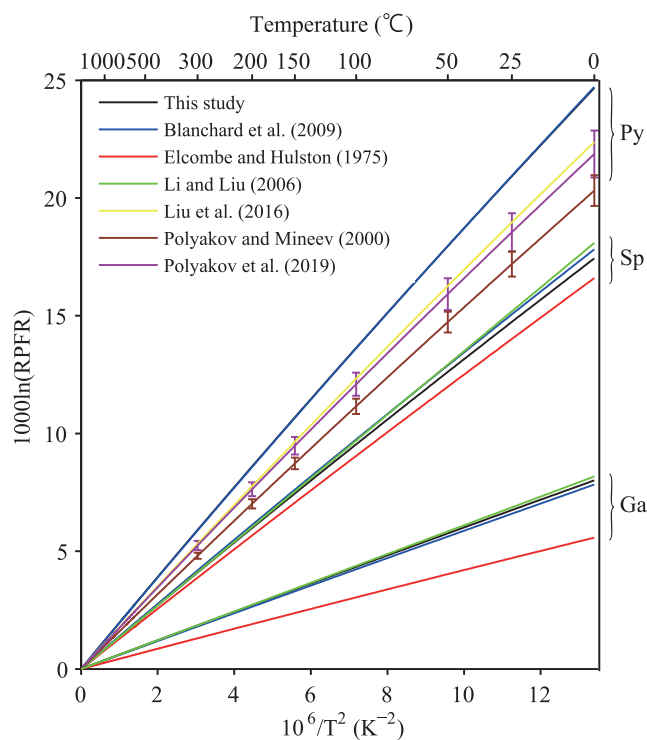


Fig. 7.  $\beta$ -factors (RPFs) of different S-bearing minerals as a function of temperature with the theoretical level B3LYP/6-311G(d). The RPFs of pyrite obtained by this study and Blanchard *et al.* have identical values. Py, Sp and Ga represent pyrite, sphalerite and galena, respectively.

and pyrite) obtained in this study and previous studies are shown in Fig. 7 and Table 4. The  $\beta$ -factors were obtained through the VVCM (cluster method) by Gaussian software. For all the sulfides, no scaling factors were used when calculating  $\beta$ -factors. Scaling factors were not used for two reasons. One reason is that scaling factors can be eliminated when calculating equilibrium isotope fractionation factors; on the other hand, simple harmonic vibration frequencies calculated by the cluster method are difficult to correct to the experimental frequency, and the experimental frequencies are not very accurate for calculating scaling factors. In the case of the  $\beta$ -factor for pyrite, the result in this study completely overlaps (the uppermost line in Fig. 7) with the result of Blanchard *et al.*, while it is different from the results of Polyakov and Mineev (2000) and Polyakov *et al.* (2007). Polyakov's team has also performed much follow-up work on this difference in pyrite. In their latest article about the  $\beta$ -factor of pyrite (Polyakov *et al.*, 2019), their result is quite different from previous results but agrees well with the calculation result of Liu *et al.* (2015). However, there is still a difference between the two sets of data for the  $\beta$ -factor of pyrite. This may be because pyrite is a disulfide,



Table 4. Polynomial expansions of the  $^{34}\text{S}/^{32}\text{S}$   $\beta$ -factors of different sulfides based on the function  $10^3 \ln \beta = ax + bx^2 + cx^3$ , with  $x = 10^6/T^2$  ( $T$  is the temperature in Kelvin)

Solids	Reference	Coefficients of the polynomial expansion: $10^3 \ln \beta = ax + bx^2 + cx^3$ $x = 10^6/T^2$ (Kelvin temperature)		
		a	b	c
Pyrite	This study	1.9726	$-10.9582 \times 10^{-3}$	$8.4091 \times 10^{-5}$
	Blanchard <i>et al.</i> (2009)	1.9617	$-9.5397 \times 10^{-3}$	$6.0390 \times 10^{-5}$
	Polyakov and Mineev (2000)	1.5997	$-6.7744 \times 10^{-3}$	$3.8254 \times 10^{-5}$
	Polyakov <i>et al.</i> (2019)	1.7532	$-1.0470 \times 10^{-2}$	$1.0424 \times 10^{-4}$
Galena	This study	0.6109	$-1.0293 \times 10^{-3}$	$0.2716 \times 10^{-5}$
	Blanchard <i>et al.</i> (2009)	0.5953	$-0.8524 \times 10^{-3}$	$0.2135 \times 10^{-5}$
	Elcombe and Hulston (1975)	0.4311	$-0.6345 \times 10^{-3}$	$0.3267 \times 10^{-5}$
Sphalerite	This study	1.3611	$-4.7807 \times 10^{-3}$	$2.2237 \times 10^{-5}$
	Blanchard <i>et al.</i> (2009)	1.3907	$-4.8719 \times 10^{-3}$	$2.2996 \times 10^{-5}$
	Elcombe and Hulston (1975)	1.3136	$-5.6876 \times 10^{-3}$	$3.0173 \times 10^{-5}$

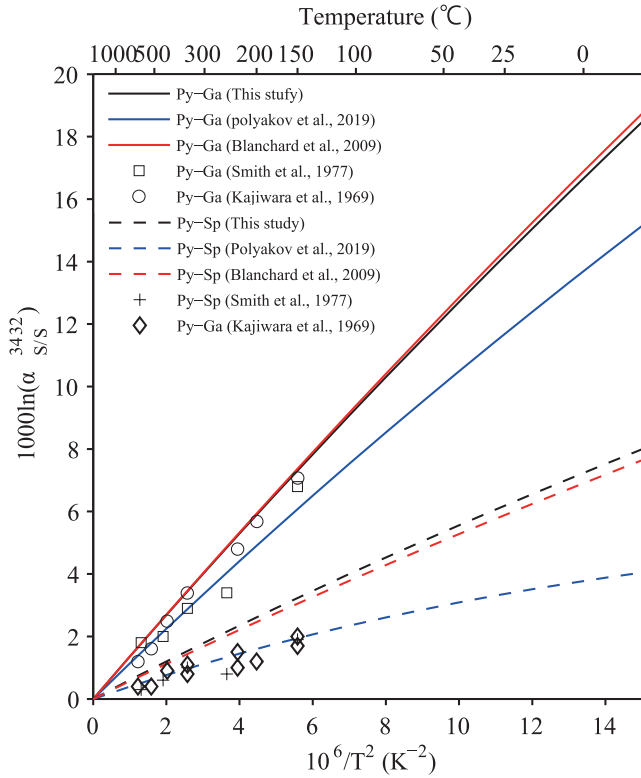


Fig. 8. Isotope fractionation factors of sulfur for pyrite-galena and pyrite-sphalerite as a function of temperature. The lines in black, blue and red are the results obtained in this study, Polyakov *et al.* and Blanchard *et al.*, respectively.

which is special. There are differences between the methods used by these studies. Taking 100°C as an example, the  $1000 \times \ln \beta$  data in this study and the studies by Blanchard *et al.* (2009) (scaling factor  $1.015 \pm 0.012$ ),

Polyakov and Mineev (2000), Polyakov *et al.* (2019) and Liu *et al.* (2015) (scaling factor 1.028) are 13.6328, 13.6189, 11.1535, 12.0897 and 12.3264, respectively. This study and Blanchard *et al.* (2009) give results that are approximately 1.3~1.5‰ higher than those of Polyakov *et al.* (2019) and Liu *et al.* (2015). The  $\beta$ -factors of other S-bearing minerals (galena and sphalerite) obtained in this study are in good agreement with the results of previous studies (see Fig. 7). The results in this study can be compared with the results in these other studies. Li and Liu (2006) used the modified increment method to calculate the reduced partition function ratio of sphalerite and galena. From Fig. 6, we know that the  $\beta$ -factor of sphalerite obtained in this study is slightly smaller than that of Blanchard *et al.* (the situation is reversed in the case of galena), but this difference is small enough. In the Blanchard *et al.* (2009) study, scaling factors of  $1.071 \pm 0.020$  ( $2\sigma$ ) and  $1.116 \pm 0.020$  ( $2\sigma$ ) were used to calculate the  $\beta$ -factors of sphalerite and galena, respectively. This may be the reason that the difference occurs. However, the results of Elcombe and Hulston (1975), which were obtained by lattice dynamics, are different from the above several studies. The lattice dynamics method gives a smaller  $\beta$ -factor than the DFT method for both sphalerite and galena. The difference for sphalerite is smaller than that for galena. In general, this study's results are in great agreement with the results of Blanchard *et al.* and Li and Liu (2006).

#### Isotope fractionation factors of sulfur for mineral pairs of pyrite-sphalerite and pyrite-galena

This study obtained the isotope fractionation factors of sulfur for mineral pairs of pyrite-galena, pyrite-sphalerite and sphalerite-galena. The temperature dependences of these factors are shown in Fig. 8 (pyrite-

galena and pyrite-sphalerite) and Fig. 6 (sphalerite-galena). This data can be compared with the theoretical and experimental results obtained by previous researchers. For  $^{34}\text{S}/^{32}\text{S}$  isotope fractionation of mineral pair of pyrite-galena, this data and the data of Blanchard *et al.* are in good agreement (Fig. 8). In addition, comparisons between theoretical and experimental data show reasonable agreement. These data match the experimental results of Kajiwara *et al.* (1969) and Smith *et al.* (1977) very well. Taking the data at 150°C as an example, the calculation result in this study is 7.30, and the two experimental results of the aforementioned previous studies are 7.1 and 6.8, respectively, which are still in good agreement. Figure 7 shows that the data at other temperatures also fit very well with the experimental results. In detail, this work's  $^{34}\text{S}/^{32}\text{S}$  fractionation factor data for pyrite-galena is slightly smaller than the data of Blanchard *et al.* This small difference is related to the  $\beta$ -factor of galena obtained in this study and in the Blanchard *et al.* study because different methods are used; in addition, the scaling factor is used in one study, but not the other, as mentioned previously. In the temperature range of 150~600°C, the data of Polyakov *et al.* (2019) also have good agreement with experimental data (Kajiwara *et al.*, 1969; Smith *et al.*, 1977). However, the results of the theoretical calculation between this study and the studies of Blanchard *et al.* (2009) and Polyakov *et al.* (2019) still have a considerable difference. Polyakov *et al.* obtained the  $\alpha_{\text{py-Ga}}$  from their data ( $\beta$ -factor of pyrite) and the data of Elcombe and Hulston (1975) ( $\beta$ -factor of galena). Their result is derived from different approaches. In theoretical calculations, calculation methods are required to be consistent before and after. In the case of the pyrite-sphalerite mineral pair, the results of this study and the study of Blanchard *et al.* (2009) are larger than the experimental data. However, the theoretical calculation result of Polyakov *et al.* (2019) matches the experimental data very well. The reason is same as the mineral pair of pyrite-galena. The data in this study can reproduce the result of Blanchard *et al.* (2009).

## CONCLUSIONS

This study uses the ab initio and DFT methods to optimize the structures and calculate the frequencies of a series of S-bearing minerals and solutions to determine RPFs of their different isotopologues and then calculates the equilibrium isotope fractionation factors between these substances.

Previous studies have investigated the  $\beta$ -factors of different sulfur-bearing minerals with different methods. In this article, the volume variable cluster model method (VVCMM) was used to re-calculate the  $\beta$ -factors of some S-bearing minerals, such as sphalerite, galena and pyrite.

Divergence mainly exists between Polyakov *et al.* and Blanchard *et al.*, and this study's results agree with the latter very well. In other words, this article provides another opinion on the magnitude of  $\beta$ -factors for sphalerite, galena and pyrite. Experimental results show that the VVCMM method is a feasible way to calculate solids. In addition, the results of the  $\beta$ -factors of  $\text{HS}^-_{(\text{aq})}$  and  $\text{H}_2\text{S}_{(\text{aq})}$  were similar to the results of previous studies.

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