

Calculation of sulfur isotope fractionation in sulfides

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Abstract

The increment method has been successfully applied to calculate thermodynamic isotope fractionation factors of oxygen in silicates, oxides, carbonates, and sulfates. In this paper, we modified the increment method to calculate thermodynamic isotope fractionation factors of sulfur in sulfides, based on chemical features of sulfur–metal bonds and crystal features of sulfide minerals. To approximate the bond strength of sulfides, a new constant, known as the Madelung constant, was introduced. The increment method was then extended to calculate the reduced partition function ratios of sphalerite, chalcopyrite, galena, pyrrhotite, greenockite, bornite, cubanite, sulvanite, and violarite, as well as the isotope fractionation factors between them over the temperature range from 0 to 1000 °C. The order of ³⁴S enrichment in these nine minerals is pyrrhotite > greenockite > sphalerite > chalcopyrite > cubanite > sulvanite > bornite > violarite > galena. Our improved method constitutes another model for calculating the thermodynamic isotope fractionation factors of sulfur in sulfides of geochemical interest.

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1. Introduction

The use of stable isotope fractionations to estimate the temperature of formation of minerals in geochemical systems has been well established by experiment or theoretical calculation, since the work of Urey and Greiff (1935) and Urey (1947) on isotopic exchange equilibria and the thermodynamic properties of substances.

Experimental measurements of sulfur isotopic fractionations among sulfides had been carried out by many researchers (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). Most of these studies have dealt with PbS, ZnS, FeS, FeS₈, and CuFeS₂. Although the results from various authors are slightly different, the sulfur isotopic fractionations in the PbS–ZnS–FeS₂ system appear to be well determined (Smith et al., 1977).

In contrast, few theoretical calculations on sulfides have been reported other than those by Sakai (1968), Groves et al. (1970), and Elcombe and Hulston (1975). Furthermore, the β -factors of ZnS and PbS calculated by the three authors are not consistent with each other, and the fractionation factors, α , calculated based on these β -factors are not consistent with those that have been determined by experiment. In addition, there exist relatively large discrepancies in the fractionation data from the same sulfide pairs from different studies.

The problems in calculating isotopic fractionation in solid minerals have been well reviewed by McLachlan (1974) and Hulston (1978), Clayton and Kieffer (1991) and Chacko et al. (2001). O'Neil (1977, 1986) pointed out that isotope fractionations in solids depended primarily on the nature of the bonds between the atoms of an element and the nearest atoms in the crystal. Also the masses of the bonding partners have an effect on isotope fractionations. Based on bond strength of the minerals, Bachinski (1969) predicted the fractionation sequence among various sulfides qualitatively and the listed sequence is supported by natural observations. Garlick (1966) and Taylor (1968) found that the degree of ¹⁸O-enrichment in

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cogenetic silicate minerals was quantitatively correlated with bond strength in silicate minerals and could be used to estimate the oxygen isotopic fractionations in silicate minerals. Schütze (1980, 1986) took into account the effects of bond strength and cation masses on isotopic substitution and developed an idea called the increment method to quantitatively calculate oxygen isotope fractionations in silicate minerals. Richter and Hoernes (1988) averaged the literature data of water β -factors and quartz–water α -factors to improve the increment method, but the calculated fractionations only in part match existing experimental data. Hoffbauer et al. (1994) used the high-temperature experimental calibration of Clayton et al. (1989) for fractionation factors between quartz and calcite as the reference system to further refine the increment method. The calculated sequence for the silicates of the same structural type is reasonable. Tao and Yuzhuo (1997) used this method to calculate fractionation factors for REE oxides. Zheng further improved the increment method and calculated the oxygen isotope fractionation factors between metal oxides (1991), wolframite (1992), anhydrous silicate minerals (1993a), hydroxyl-bearing silicates (1993b), SiO₂ and Al₂-SiO₅ polymorphs (1993c), perovskite (1994), magnetites (1995a), TiO₂ polymorphs (1995b), uranium oxides (1995c), zinc oxides (1996a), apatites (1996b), hydroxides (1998), and carbonates and sulfates (1999). Zheng's results are fairly consistent with those from experimental data. Therefore, it is interesting to attempt to calculate the isotope fractionations between sulfides using the increment method.

In this paper, the increment method has been modified to calculate the reduced partition function ratios of sphalerite, chalcopyrite, galena, pyrrhotite, greenockite, bornite, cubanite, sulvanite, violarite, and the isotope fractionation factors between them over a temperature range from 0 to 1000 °C, based on chemical features of sulfur–metal bonds and crystal features of sulfides. To approximate the bond strength of sulfides, a new constant called the Madelung constant was introduced in our calculation.

2. Calculation method and results

Our calculation is based on the increment method by Schütze (1980, 1986) for oxygen isotope fractionation in silicate minerals and an improved version by Zheng (1991) for metal oxides.

According to the method, to calculate the β -factor of a sulfide in question, it is necessary to select a sulfide and a bond in this sulfide as the reference mineral and the reference bond, plus the β -factor of this reference sulfide. Then, the degree (I–³⁴S) of ³⁴S enrichment of a sulfide in question is computed by comparing the ³⁴S-increment of the bonds in this sulfide to that of the reference bond in the reference sulfide. In this study, sphalerite and Zn–S bond are selected as the reference mineral and the reference bond, respectively, and the mineral pair sphalerite and galena is used to calculate the β -factor of sphalerite using the method of

Schütze (1980). The experimental data of the fractionations in the PbS–ZnS–FeS₂ system are well established (Smith et al., 1977), so this system can be used to assess the theoretically calculated values.

In this paper, the β -factor of the sulfide in question is calculated by¹

$$10^3 \ln \beta_{\text{Min}} = I^{-34}S_{\text{Min}} \cdot 10^3 \ln \beta_{\text{Sp}}, \quad (1)$$

where $I^{-34}S_{\text{Min}}$ is defined by

$$I^{-34}S_{\text{Min}} = \frac{(M_{32}/M_{34})_{\text{Sp}}^{3/2}}{n_{\text{ch}}n_{\text{s}}(M_{32}/M_{34})_{\text{Min}}^{3/2}} \cdot \frac{\sum_1^{n_{\text{ct}}} i_{\text{ct-S}} \cdot V}{i_{\text{Zn-S}}} \quad (2)$$

the ³⁴S-increment of a cation–sulfur bond $i_{\text{ct-S}}$ is calculated from

$$i_{\text{ct-S}} = \frac{V}{(r_{\text{ct}} + r_{\text{s}})\text{CN}_{\text{ct}}} \cdot \ln \sqrt{\frac{m_{\text{ct}} + m_{32}}{m_{\text{ct}} + m_{34}} \cdot \frac{m_{34}}{m_{32}}} \cdot \frac{C_{\text{m}}}{\text{CN}_{\text{ct}}}, \quad (3)$$

where subscripts Sp and Min denote sphalerite and the sulfide in question, respectively; ct, s, and ch denote the cation in question, S anion and charge, respectively; Zn–S and ct–S denote the Zn–S bond and the bond between the sulfur anion and the metal ion; n_{ch} is the charge number of the sulfur anion; n_{s} and n_{ct} are the number of sulfur anions and the number of cations per formula unit, respectively; M_{32} and M_{34} are the sulfide masses of the lighter (³²S) and the heavier (³⁴S) isotopic form; CN_{ct} is the coordination number of the cation; V is the oxidation state of the cation; C_{m} is the Madelung constant; m_{ct} , m_{32} , and m_{34} are the atomic weights of the cation, ³²S and ³⁴S isotopes, respectively; r_{ct} and r_{s} are the radii of the cations and sulfur anion at this coordination number of the sulfide.

To approximate the value of $i_{\text{ct-S}}$ more exactly, a constant C_{m} is introduced to calculate the bond strength of sulfides with different crystalline structures, based on the sulfide crystal chemistry. The reason to introduce this constant in our calculation will be discussed later.

The present calculation deals with the following sulfides: sphalerite, chalcopyrite, galena, pyrrhotite, greenockite, bornite, cubanite, sulvanite, and violarite. The crystal structures of these sulfides and their ionic radii are after Zoltai and Stout (1984). The parameters used and the calculated $i_{\text{ct-S}}$ values for these nine sulfides are listed in Table 1.

The published experimental and theoretical studies (Smith et al., 1977; Ohmoto and Rye, 1979; Hubberten, 1980) on sulfide isotope exchanges indicate that the magnitude of fractionation factors between sulfides depends primarily on temperature, becoming smaller with increasing temperature (Ohmoto and Goldhaber, 1997), whereas pressure seems to play no significant role. Thus, the

¹ A temperature correction term D (introduced by Zheng, 1991; based on the transport property of matter) is not introduced in Eq. (1), because it is an empirical term of low-temperature correction for oxygen-bearing minerals. Zheng (1991) added this term to raise the β -factors of an oxide at low temperatures below 250 and 300 °C, otherwise the calculated values are too low in this temperature range with respect to the known results.

Table 1
Calculated i_{ct-s} values for the nine sulfides based on Eq. (3)

Bond	CN _{ct}	CN _S	$r_s + r_{ct}(\text{Å})$	m_{ct}	C_m	i_{ct-s}
Zn ²⁺ -S ²⁻	4	4	2.24	65.37	1.638055	0.00184
Pb ²⁺ -S ²⁻	6	6	2.98	207.19	1.747565	0.00085
Fe ²⁺ -S ^{2-a}	6	6	2.50	55.85	4.816	0.00203
Cu ²⁺ -S ²⁻	4	4	2.26	63.55	1.638055	0.00180
Fe ²⁺ -S ²⁻	4	4	2.27	55.85	1.638055	0.00171
Cd ²⁺ -S ²⁻	4	4	2.44	112.4	1.641322	0.00197
Cu ¹⁺ -S ²⁻	4	4	2.16	63.55	1.638055	0.00094
Fe ³⁺ -S ²⁻	4	4	2.13	55.85	1.638.55	0.00274
V ²⁺ -S ²⁻	4	4	2.43	50.94	1.641322	0.00155
Ni ³⁺ -S ^{2-a}	6	6	2.38	58.71	1.747465	0.00118

^a Here mean ionic radii of in high spinning and low spinning states are taken for calculation.

experimental fractionation factors α between sulfides are only a function of temperature, and $10^3 \ln \beta_{\text{Min}}$ can be defined by

$$10^3 \ln \beta_{\text{Min}} = A \times 10^6 / T^2, \quad (4)$$

where the subscript Min means sulfides in question. The most reliable experimental results between sphalerite and galena are at 473 K, so based on Schütze (1980), $10^3 \ln \beta_{\text{Sp}}(T)$ can be calculated by

$$10^3 \ln \beta_{\text{Sp}}(T) = \frac{I_{34s}^{\text{Sp}} \cdot \Delta\delta^{34}\text{S}^{\text{Sp-Ga}}(473 \text{ K})}{I_{34s}^{\text{Sp}} - I_{34s}^{\text{Ga}}} \cdot \frac{473^2}{10^6} \cdot \frac{10^6}{T^2}, \quad (5)$$

where Sp and Ga denote sphalerite and galena, respectively. $\Delta\delta^{34}\text{S}^{\text{Sp-Ga}}(473 \text{ K})$ can be approximated by

$$10^3 \ln \alpha = A \times 10^6 / T^2. \quad (6)$$

In this calculation, a value of 0.74 (Smith et al., 1977) is used for the coefficient A in Eq. (6), and $10^3 \ln \beta_{\text{Sp}}(T)$ is then given by

$$10^3 \ln \beta_{\text{Sp}} = 1.35 \cdot \frac{10^6}{T^2}. \quad (7)$$

Table 2 lists the calculated $I^{-34}\text{S}$ indexes and $10^3 \ln \beta$ values of these sulfides. As shown in Table 2, a significant difference between isotopic fractionation behaviors of sulfur in sphalerite and galena is indicated by the greater

Table 2
Calculated $I^{-34}\text{S}$ indexes and $10^3 \ln \beta$ values of the nine sulfides based on Eqs. (2) and (1), respectively

Sulfide	Chemical formula	$\frac{(M_{32}/M_{34})_{\text{Sp}}^{3/2}}{(M_{32}/M_{34})_{\text{min}}^{3/2}}$	$I^{-34}\text{S}$	$10^3 \ln \beta = A \cdot T^2/10^6$
Sphalerite	ZnS	1.00000	1.0000	$1.35 \cdot T^2/10^6$ ^a
Galena	PbS	0.98217	0.4537	$0.61 \cdot T^2/10^6$ ^b
Chalcopyrite	FeCuS ₂	1.00187	0.9610	$1.30 \cdot T^2/10^6$ ^b
Pyrrhotite	FeS	1.00327	1.1123	$1.50 \cdot T^2/10^6$ ^b
Greenockite	CdS	0.9902	1.0602	$1.43 \cdot T^2/10^6$ ^b
Bornite	Cu ₅ FeS ₄	0.9934	0.8772	$1.18 \cdot T^2/10^6$ ^b
Sulvanite	Cu ₃ VS ₄	1.0016	0.9499	$1.28 \cdot T^2/10^6$ ^b
Cubanite	CuFe ₂ S ₃	1.0023	0.9533	$1.29 \cdot T^2/10^6$ ^b
Violarite	FeNi ₂ S ₄	1.0086	0.7251	$0.98 \cdot T^2/10^6$ ^b

^a Calculated by Eq. (5) based on the experimental data from Smith et al. (1977).

^b Calculated by Eq. (1) based on the $10^3 \ln \beta$ value of Sphalerite.

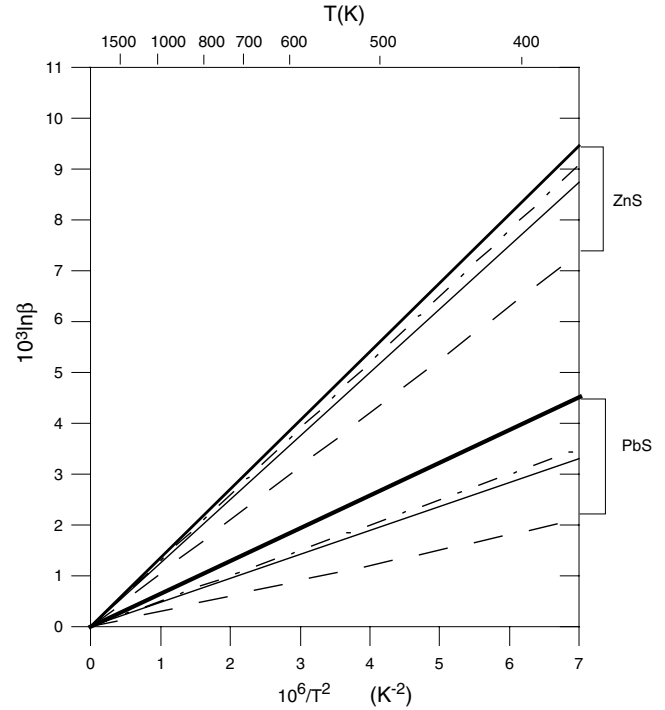


Fig. 1. Comparison of the $10^3 \ln \beta$ values for sphalerite and galena. Black full line represents the calculation presented in this paper; dot-dash line by Sakai (1968); dash line by Groves et al. (1970); full-line by Elcombe and Hulston (1975).

$I^{-34}\text{S}$ index for sphalerite than that for galena due to the differences in their crystal structure and cation distribution.

For comparison, we also show the calculated $10^3 \ln \beta$ data for ZnS and PbS of the present calculation and the previous theoretical calculations by Sakai (1968), Groves et al. (1970), and Elcombe and Hulston (1975) in Fig. 1. As shown in Fig. 1, discrepancies exist between the present calculation and the previous calculation, with this calculation being slightly higher than the previous. However, the previous calculated results are also not inconsistent with each other (Elcombe and Hulston, 1975).

The $10^3 \ln \alpha$ values between different minerals can be calculated by

$$10^3 \ln \alpha_{x-y} = 10^3 \ln \beta_x - 10^3 \ln \beta_y. \quad (8)$$

Except the systematic errors from the model for calculating $I^{-34}\text{S}_{\text{min}}$ values of minerals and the model for calculating the $10^3 \ln \beta$ value of sphalerite, the difference in $\Delta\delta^{34}\text{S}^{\text{Sp-Ga}}$ value between the theoretically calculated value using Eq. (5) and the experimentally measured value by Smith et al. (1977) is about $\pm 1\%$. So the uncertainties of the present calculated fractionation factors between these nine sulfides are within $\pm 2\%$.

3. Discussion

Previous studies on the isotope fractionation factors of sulfides have mainly dealt with the ZnS–PbS–FeS₂ system

(Grootenboer and Schwarcz, 1969; Kajiwarra et al., 1969; Rye and Czamanske, 1969; Kajiwarra and Krouse, 1971; Salomons, 1971; Czamanske and Rye, 1974), the sulfide–S system (Hubberten, 1980; Bente and Nielsen, 1982) and the sulfide–H₂S system (Ohmoto and Rye, 1979; Ohmoto and Goldhaber, 1997). Furthermore, the literature data of 10³ ln β for other sulfides in addition to PbS and ZnS are unavailable. So we cannot make direct comparison between our results and others.

If two independent fractionation equations contain one identical phase, it is common practice to combine both equations into a new equation that directly relates the other two phases. The equation is given below among three minerals A, B, and C.

$$10^3 \ln \alpha_{A-C} = 10^3 \ln \alpha_{A-B} - 10^3 \ln \alpha_{B-C}. \quad (9)$$

We can use the experimental data of sulfide–H₂S (Ohmoto and Rye, 1979; Ohmoto and Goldhaber, 1997) to calculate fractionation factors between these nine sulfides based on Eq. (9). Table 3 gives the comparison between the indirectly derived results by Eq. (9) and our results based on Eq. (8). For convenience, Table 4 lists the sulfur isotope fractionations of these nine sulfides with respect to H₂S based on Eq. (8) and those available from Ohmoto and Goldhaber (1997), and the comparison is also expressed graphically in Fig. 2. Here, the 10³ ln β value of H₂S is calculated using the 10³ ln β value of ZnS based on Eq. (8).

As shown in Tables 3 and 4 and Fig. 2, there are some discrepancies between the present calculations based on Eq. (8) and the estimates of equilibrium isotopic fractionation factors of sulfides after Ohmoto and Goldhaber (1997) based on Eq. (9). In fact, there appears to be a systematic discrepancy. Our results are always slightly more negative than the estimates by Eq. (9), in addition to sulfide pairs involving cubanite and pyrrhotite–chalcopyrite. With respect to pyrrhotite–chalcopyrite, the experimental calibration data of Zn–H₂S and PbS–H₂S by Ohmoto and Rye (1979) given in Fig. 2 and Table 4 show that there is no isotope fractionation between sphalerite and pyrrhotite. And in turn, the derived results for pyrrhotite–chalcopyrite and sphalerite–chalcopyrite based on Eq. (9) are the same. This is certainly inconsistent with

Table 4
Equilibrium isotopic fractionation factors of sulfides with respect to H₂S from the present calculation and from Ohmoto and Goldhaber (1997)

Sulfides	The coefficient <i>A</i> in Eq. (6)	
	<i>A</i> (this calculation)	<i>A</i> (Ohmoto and Goldhaber)
Sphalerite	0.10	0.10
Galena	−0.64	−0.63
Pyrrhotite	0.25	0.10
Chalcopyrite	0.05	−0.05
Greenockite	0.18	−0.4
Bornite	−0.07	−0.25
Cubanite	0.04	0.05
Violarite	−0.27	
Sulvanite	0.03	

Here, the 10³ ln β value for H₂S is 1.25 × 10⁶/T², which can be calculated by Eq. (8) using the 10³ ln β value for ZnS.

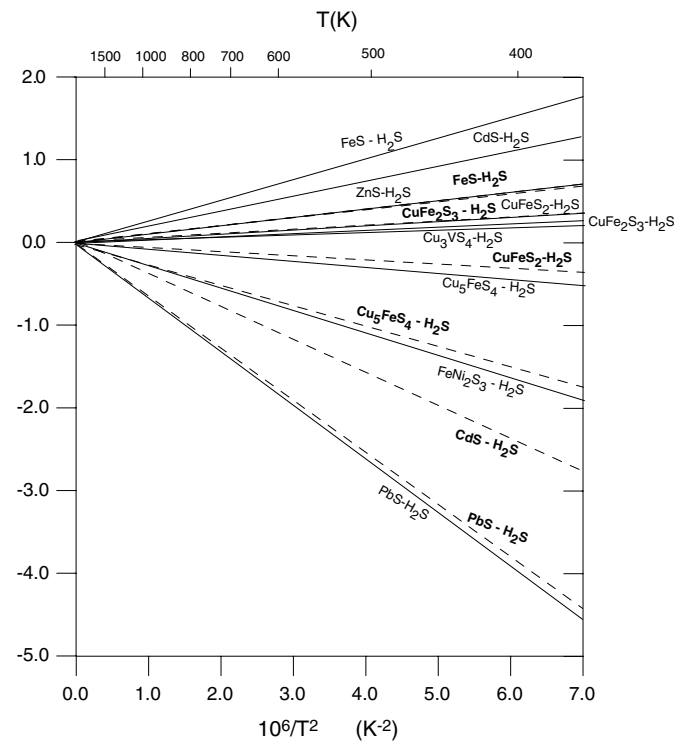


Fig. 2. Equilibrium isotopic fractionation factors of sulfides with respect to H₂S from this calculation and from Ohmoto and Goldhaber (1997); full line by this calculation, and dash line from Ohmoto and Goldhaber (1997).

Table 3
The coefficients *A* calculated by Eqs. (8) and (9), respectively

	Sphalerite		Galena		Pyrrhotite		Chalcopyrite		Greenockite		Bornite		Cubanite		Violarite		Sulvanite		
	<i>A</i> (8)	<i>A</i> (9)	<i>A</i> (8)	<i>A</i> (9)	<i>A</i> (8)	<i>A</i> (9)	<i>A</i> (8)	<i>A</i> (9)	<i>A</i> (8)	<i>A</i> (9)	<i>A</i> (8)	<i>A</i> (9)	<i>A</i> (8)	<i>A</i> (9)	<i>A</i> (8)	<i>A</i> (9)	<i>A</i> (8)	<i>A</i> (9)	
Sphalerite					−0.15	0	0.05	0.15	−0.08	0.5	0.17	0.35	0.06	0.05	0.37			0.07	
Galena					−0.89	−0.73	−0.69	−0.58	−0.82	−0.23	−0.57	−0.38	−0.68	−0.68	−0.37			−0.67	
Pyrrhotite							0.20	0.15	0.07	0.5	0.32	0.35	0.21	0.05	0.52			0.22	
Chalcopyrite									−0.13	0.35	0.12	0.2	0.01	−0.10	0.32			0.02	
Greenockite											0.25	−0.15	0.14	−0.45	0.45			0.15	
Bornite													−0.11	−0.3	0.30			−0.10	
Cubanite															0.31			0.01	
Violarite																			
Sulvanite																			−0.30

“*A*” refers to the isotope fractionation coefficient *A* in equation 10³ ln α = *A* × 10⁶/T², 8 and 9 indicate result calculated by using Eqs. (8) and (9), respectively.

observations in nature (Bachinski, 1969). Criss (1999) commented that derived fractionation equations will have larger uncertainties than the original determinations. Moreover, their range of validity may be very restricted, making extrapolations dangerous. On the other hand, our results would predict a small isotope fractionation between sphalerite and pyrrhotite ($A = -0.15$, in Table 3) that seems to be more consistent with observations in nature (Bachinski, 1969).

As to cubanite, the fractionation factors between cubanite and other sulfides are slightly higher than the derived estimates by Eq. (9) given in Table 3. The main reason may be that there exists significant difference between the crystal structure of cubanite [Stacking structure $A(\frac{11}{22})B(\frac{11}{22})$] and that of sphalerite [Stacking structure $A(-1-)B(-1)C(1-)$], which made the uncertainty of the increment calculations larger. One of the main aspects of the increment method is that isotopic fractionation properties are calculated in increments from a reference mineral (Zheng, 1993b). Nevertheless, even if a given model cannot predict isotopic fractionation factors for every mineral with high accuracy, it can be useful in providing a basis for understanding fractionation behavior in minerals with the same structure type and for extrapolation of existing data.

In the present calculation, the order of ^{34}S enrichment in these nine minerals is pyrrhotite > greenockite > sphalerite > chalcopyrite > cubanite > sulvanite > bornite > violarite > galena, which is slightly different from the literature data. But in view of the discrepancies of sulfur isotope fractionation literature data about the same sulfide pairs from different researchers, and the difficulty to experimentally measure and theoretically calculate the fractionation factor between sulfides, the present calculation can be viewed as another approximate method.

3.1. The complexity of sulfides

Our calculation is based on the increment method by Schütze (1980, 1986) for oxygen isotope fractionation in silicate minerals and an improved version by Zheng (1991) for metal oxides. However, sulfides are more complex than oxides, because unlike elemental O, elemental S has different oxidation states (e.g., the oxidation state in pyrrhotite and pyrite for S is different, even though both minerals are composed of Fe and S). Sulfides have a broad range of structures because of the large number of possible coordination polyhedra between metals and sulfur. Furthermore, unlike the oxides in which chemical bonding is predominantly ionic, most of the bonding in the sulfide minerals is covalent or metallic, or both. In addition, the ratio of S to metal is easily changeable and form non-stoichiometric structures in some sulfides, which make accuracy calculation more difficult.

3.2. The $10^3 \ln \beta$ value of pyrrhotite

Pyrrhotite has a non-stoichiometric structure and some unusual characteristics. Firstly, it has an unusual formula. Secondly, it has two symmetries. When pyrrhotite is low in sulfur and the formula is closer to true FeS, the structure is hexagonal. But when it is high in sulfur the structure is monoclinic. Clearly two different symmetries and two different formulae, typically characterize two different minerals, but a natural pyrrhotite sample often contains both crystal phases. This may be the main reason for the isotopic fractionation discrepancies between experimental values and theoretically calculated values.

According to the increment method, the $10^3 \ln \beta$ value depends mainly on the number of cations that bond with S. But there are vacancies for the Fe cation in the crystal lattice of pyrrhotite, and in order to balance the electrovalence, bonds between S atoms must exist. These may also have some influence on the fractionation. Furthermore, the number of the vacancies varies with different ratios of S to Fe. Therefore, an approximation is needed for our calculation. In our present calculation we use the molecular formula of FeS to approximate the molecular formula of pyrrhotite, and the calculated results seems reasonable.

The other factor that influences the $10^3 \ln \beta$ value of pyrrhotite is the spinning state of FeS which affects the radii of Fe cation in our present calculation. In the above calculation, the value of the radius of Fe is taken as the average radii in the low spinning state and in the high spinning state. Table 5 lists the maximum value of $10^3 \ln \beta$ and the minimum value of $10^3 \ln \beta$ in these two states, and the $10^3 \ln \beta$ data of a pyrrhotite sample is some value between $1.45 \cdot T^2/10^6$ and $1.55 \cdot T^2/10^6$. Therefore, the spinning state of Fe has less influence on the $10^3 \ln \beta$.

3.3. Madelung constant

Differences in electronegativity between oxygen and sulfur lead to different bond characteristics between sulfide and oxide minerals. Oxygen is more electronegative, and would be expected to form bonds with ionic character, while sulfur is less electronegative and forms bonds with covalent or metallic character, or both. Covalent bonds take on direction characteristics, and if two elements form bonds in the same direction, the bond strength is greater. Furthermore, sulfides have a broad range of structures because of the large number of possible coordination polyhedra between metals and sulfur. Crystal structure characteristics of sulfides seem to have more influence on

Table 5
 $I\text{-}^{34}\text{S}$ values at different spinning states of elemental Fe

Spinning state	$r_s + r_{ct}$ (Å)	$10^3 \ln \beta_{\text{Pyrr}}$ A
Low	2.41	1.55
High	2.58	1.45

Pyrr, pyrrhotite.

Table 6
Calculated $10^3 \ln \beta$ values of the nine sulfides without the Madelung constant

Sulfide	Chemical formula	$10^3 \ln \beta$	
		A (with M)	A (without M)
Sphalerite	ZnS	1.35 ^a	2.02 ^a
Galena	PbS	0.61 ^b	1.28 ^b
Chalcopyrite	FeCuS ₂	1.30 ^b	1.95 ^b
Pyrrhotite	FeS	1.50 ^b	1.14 ^b
Greenockite	CdS	1.43 ^b	2.13 ^b
Bornite	Cu ₅ FeS ₄	1.18 ^b	1.77 ^b
Sulvanite	Cu ₃ VS ₄	1.28 ^b	1.92 ^b
Cubanite	CuFe ₂ S ₃	1.29 ^b	1.93 ^b
Violarite	FeNi ₂ S ₄	0.98 ^b	1.86 ^b

Here, data in the last column were calculated based on Eqs. (1)–(3) without the Madelung constant.

^a Calculated data by Eq. (5) based on the experimental data from Smith et al. (1977).

^b Calculated data by Eq. (1) based on the $10^3 \ln \beta$ data of Sphalerite.

bond strength than do those of oxides. Therefore in comparison with oxides, some parameters should be added to the increment method to distinguish the differences in bond strength that are related to the different structures of sulfides.

In mineralogy, the Madelung constant (denoted by C_m in Eq. (3)) can be used to demonstrate that a collection of ions bonded together in an orderly array possesses a lower energy than a random array of isolated atoms, and their energy depends on the particular geometry of ions in the crystal (Zoltai and Stout, 1984). The Madelung constant is a geometrical factor, whose value depends on the arrangement of ions in the solid. So it is possible to distinguish the relative bond strengths of sulfides due to their structure differences using the Madelung constant.

Table 6 lists $10^3 \ln \beta$ values for nine sulfides calculated without the Madelung constant in Eq. (3), and for comparison the calculated $10^3 \ln \beta$ values of these sulfides with the Madelung constant are also listed in Table 6. There exist very significant differences between these two groups of data. As shown in Table 6, without the Madelung constant in Eq. (3), the $10^3 \ln \beta$ value for pyrrhotite is very small and shows the lowest enrichment of ^{34}S , and the $10^3 \ln \beta$ values for ZnS and PbS are much larger than those calculated from data available in the literature. This pattern is not consistent with the experimental data and observations in nature. But by adding a Madelung constant C_m in Eq. (3), the results are consistent with natural and experimental values. Although this procedure requires a more detailed consideration of mineral structural characteristics and could introduce systematic errors into the β factors, it seems reasonable to introduce a Madelung constant (C_m) into the present calculation to approximate the $10^3 \ln \beta$ value.

4. Conclusion

The present work extends the increment method to calculate sulfur isotope fractionation factors. The $10^3 \ln \beta$ val-

ues for sphalerite, chalcopyrite, galena, pyrrhotite, greenockite, bornite, cubanite, sulvanite, violarite and $10^3 \ln \alpha$ values between them over the temperature range from 0 to 1000 °C have been calculated. The order of ^{34}S enrichment in these nine minerals is pyrrhotite > greenockite > sphalerite > chalcopyrite > cubanite > sulvanite > bornite > violarite > galena. A significant difference for sulfur isotopic fractionation between sphalerite and galena is indicated by the greater $I^{-34}\text{S}$ index for sphalerite relative to that for galena, due to the differences in their crystal structure and cation distribution. The improvement on the increment method presented in this paper provides another approximate calculation method for sulfur isotope fractionation in sulfides.

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