**First-principles calculations of sulphur isotope fractionation in MX_2 minerals,
with $M = \text{Fe, Co, Ni}$ and $X_2 = \text{AsS, SbS}$**

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Abstract Iron, Co and Ni are first row transition metals and are all able to combine with S, As, and Sb to form disulphides, sulpharsenides and sulphantimonides, respectively, all of which exhibit substitutions of metal and metalloid elements in their structures. As an important tracer in the geochemistry of ore deposits, S isotope fractionation in sulphides can be used to analyse the ore-forming process and the source of ore-forming elements. However, there have been few studies of S isotope fractionation in sulpharsenides and sulphantimonides. Studying the isotope fractionation of the various members of this structural group can provide systematic information regarding S isotope fractionation in transition metal disulphides, sulpharsenides and sulphantimonides. In this paper, the S isotope fractionation parameters for Fe, Co and Ni sulpharsenides and sulphantimonides were calculated using first-principles methods based on density functional theory in the temperature range of 0-1000 °C. Our calculations show that the order of heavy S isotope enrichment is arsenopyrite > cobaltite > gudmundite > costibite >

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gersdorffite > ullmannite. For sulphides with the same anion pair, the main factor affecting S isotope fractionation is the metal-sulphur bond strength. For most of the sulphides studied in this paper, S isotope fractionation arising from substitution of metalloid elements is much smaller than that of metal elements.

Keywords: Sulpharsenides; Sulphantimonides; S isotope fractionation; First-principles; DFPT

1. Introduction

The sulphides are an important group of minerals, which have great economic importance as the major source of metals. Although the sulphides are much less abundant than the silicates, they include a disproportionately large number of distinct minerals because of their broad range of structure and chemistry (Zoltai and Stout, 1984). In a number of important sulphide minerals, such as the pyrite-group sulphides, the structures are quite complex because the bonding characteristics are directional. The pyrite-group minerals include derivatives of the pyrite structure MX_2 , with M = Fe, Co, Ni and X = S, Se, Te, As, or Sb (Bayliss, 1989; Berry et al., 1983; Wood and Strens, 1979). They crystallize in structures characterized by "dumbbells" of tightly bonded anion pairs (e.g., S-S, As-As, As-S or Sb-S), in which each anion has tetrahedral coordination to one anion and three cations, and each cation has octahedral coordination to six anions (Hem et al., 2001; Nickel, 1968).

The disulphides of Fe, Co and Ni (FeS_2 , CoS_2 and NiS_2) have a structure based on that of halite, with the S_2 dumbbell occupying the sites at the centre of the cubic unit cell and the mid-points of the cube edges (Vaughan and Craig, 1978), and three coordination octahedra of divalent cations meeting at each end of the S_2 dumbbell (Makovicky, 2006). Structurally, the sulpharsenides of Fe, Co and Ni ($FeAsS$, $CoAsS$, $NiAsS$) resemble disulphides (FeS_2 , CoS_2 , NiS_2)

with one of the S atoms replaced by an As atom. As the most abundant arsenic mineral and a common mineral in Pb-Zn-Ag ores, arsenopyrite (FeAsS) is commonly associated with pyrite, chalcopyrite, sphalerite, and galena, constitutes a major ore mineral in orogenic gold ores, and typically occurs as an early formed mineral at moderate to high-temperature conditions (Berry et al., 1983; Bindi et al., 2012; Costa, 2002; Zoltai and Stout, 1984). Cobaltite (CoAsS), a significant source of the strategically important metal Co (Barceloux and Barceloux, 1999; Barańkiewicz and Siepak, 1999), occurs in high temperature hydrothermal deposits and contact metamorphic rocks (Berry et al., 1983; Staude et al., 2007). Gersdorffite (NiAsS) occurs in hydrothermal vein deposits formed at intermediate temperatures (Anthony et al., 2001). These three sulpharsenides, together with other sulpharsenides such as alloclasite and glaucodot, are important members of the ternary FeAsS-CoAsS-NiAsS system (Yang and Downs, 2008). They can incorporate considerable amounts of trace metals, especially “invisible” gold when precipitated from hydrothermal solutions (Palenik et al., 2004), and can release significant amounts of arsenic into natural water and soils under oxidizing conditions, producing serious arsenic poisoning and contamination in some cases (O’Day, 2006). Therefore, some experimental and theoretical studies (Makovicky, 2006; Vaughan and Rosso, 2006) have focused on them.

Compared with the disulphides and sulpharsenides of Fe, Co and Ni, the sulphantimonides of Fe, Co and Ni (FeSbS, CoSbS, NiSbS) are relatively rare. These minerals resemble disulphides (FeS₂, CoS₂, NiS₂) with one of the S atoms replaced by an Sb atom. Gudmundite (FeSbS) occurs in some sulphide deposits (Wagner and Jonsson, 2001), Sb deposits (Normand et al., 1996), and gold deposits associated with arsenopyrite (Deschênes et al., 2009a, 2009b; Ding et al., 2014). In addition, it is associated with ferroan dolomite and pyrrhotite as early impregnations in the host

rocks at the margin of veins and in silicified fault zones (Trottier et al., 1991), and occurs mainly with gangue minerals, such as chlorite, quartz, calcite and plagioclase (Minz et al., 2013). Ullmannite (NiSbS), in association with nickeline, gersdorffite, pentlandite, chalcopyrite, pyrrhotite, galena, tetrahedrite, and dyscrasite (Anthony et al., 2001), occurs in hydrothermal deposits and can form a series in the NiSbS-CoSbS system with willyamite (Dobbe, 1991). Costibite (CoSbS), the end-member of willyamite ((Co,Ni)SbS) (Cannr et al., 1970), is found in association with paracostibite, nisbite and cobaltian ullmannite in Pb-Zn-Cu-Ag deposits, and occurs as small inclusions in galena (Zakrzewski et al., 1980).

Given all of this, it is clear that the disulphides, sulpharsenides and sulphantimonides of Fe, Co and Ni can coexist in ore deposits; this may provide an opportunity for researching the ore-forming temperature and the source of the ore-forming material through the S isotope fractionation between the phases. Additionally, studying S isotope fractionation in disulphides, sulpharsenides and sulphantimonides may provide the opportunity to examine the various members of a structural group in which only the metal atom is changed, or where one S atom is replaced by an As atom or an Sb atom, thereby providing information that permits a systematic development of concepts regarding S isotope fractionation in transition metal disulphides, sulpharsenides and sulphantimonides.

To the best of our knowledge, there are a small number of studies that have provided equilibrium S isotope fractionation factors in transition metal disulphides, sulpharsenides and sulphantimonides. Several researchers have carried out experimental measurements of fractionation between pyrite and other sulphides, such as: ZnS-PbS-FeS₂-S (Grootenboer and Schwarcz, 1969), FeS₂-ZnS-PbS (Kajiwarra et al., 1969; Smith et al., 1977),

FeS₂-CuFeS₂-PbS-ZnS (Kajiwara and Krouse, 1971), FeS₂-PbS-S (Salomons, 1971), and some sulphide minerals-H₂S system (Ohmoto and Rye, 1979; Ohmoto and Goldhaber, 1997). In contrast, theoretical calculations have not been reported except for in the studies of Polyakov et al. (2007), Blanchard et al. (2009), Polyakov and Soultanov (2011), and Liu et al. (2015). Furthermore, there are scarcely any studies on S isotope fractionation in transition metal sulpharsenides and sulphantimonides.

Recent studies have demonstrated that the first-principles calculation based on density functional theory is a powerful tool for calculating the isotope fractionation factors for a variety of isotope systems including H, O, Mg, Ca, Si, S, Fe, Ge and Se (Balan et al., 2014; Blanchard et al., 2009; Feng et al., 2014; Huang et al., 2014; Li and Liu, 2010, 2011; Liu et al., 2014, 2015; Méheut et al., 2009, 2010; Méheut and Schauble, 2014; Reynard and Caracas, 2009; Schauble, 2011; Wu et al., 2015). In this study, this approach is used to investigate the equilibrium S isotope fractionation in the sulpharsenides and sulphantimonides of Fe, Co and Ni. Specifically, we analyse the influence of metal substitution and metalloid substitution on equilibrium S isotope fractionation in the sulphides. These results are important in studying the isotope fractionation arising from more complex substitutions.

2. Calculation methods

In the present study, S isotope fractionation is assumed to be mass dependent, driven by changes of vibrational (phonon) frequencies from isotopic substitution (Bigeleisen and Mayer, 1947; Kieffer, 1982; Urey, 1947). Other potentially isotope-dependent effects on lattice energy are ignored, since they are expected to be insignificant for moderate-mass elements (Schauble, 2011). Isotopic fractionation can be considered in terms of isotopic exchange reactions, which are driven

thermodynamically toward equilibrium. Thus, between two substances AY and BY , isotopic equilibrium with one exchangeable atom of Y , can be described as following:

where Y and Y^* refer to the light and heavy isotopes of the element Y , respectively. The isotope fractionation factor of the element Y between the substances AY and BY , α_{AY-BY} , is the ratio of the reduced partition function ratios. It can also be written as:

$$\alpha_{AY-BY} = \beta_{AY} / \beta_{BY} \quad (2)$$

where β_{AY} , the reduced partition function ratio of element Y in phase AY , is the isotopic fractionation factor of the element Y between the phase AY and a perfect gas of Y atoms, having the natural mean isotopic concentration (Richet et al., 1977). If AY is a crystalline solid, β_{AY} can be calculated from its harmonic vibrational frequencies as following (Blanchard et al., 2009; Méheut et al., 2007, 2009; Méheut and Schauble, 2014):

$$\beta_{AY} = \left[\prod_{i=1}^{3N_A} \prod_{\{q\}}^* \frac{\nu_{q,i}^*}{\nu_{q,i}} \frac{e^{-h\nu_{q,i}^*/(2kT)}}{1 - e^{-h\nu_{q,i}^*/(kT)}} \frac{1 - e^{-h\nu_{q,i}/(kT)}}{e^{-h\nu_{q,i}/(2kT)}} \right]^{1/(N_q N)} \quad (3)$$

where N_A is the number of atoms in the unit-cell; N_q is the number of q -vectors in the Brillouin zone; N is the number of sites for the Y atom in the unit-cell; $\nu_{q,i}$ and $\nu_{q,i}^*$ are the frequencies of the phonon with wavevector q in two isotopically different materials and branch index $i=1, 3N_A$; T is the temperature; h is the Planck constant; and k is the Boltzmann constant. The * symbol above the product of Eq. (3) indicates that the three translational modes at the centre of the Brillouin zone with $\nu_{0,i} = 0$ and $\nu_{0,i}^* = 0$ are not considered.

Electronic structures and vibrational (phonon) frequencies of minerals are calculated using Quantum Espresso (Giannozzi et al., 2009). A spin-polarized calculation was performed to address the 3d metal ions. Generalized gradient approximations (GGA) to the exchange-correlation

functional of Perdew, Burke and Ernzerhof (PBE) (Perdew et al., 1996) were used. Ionic cores of each atom are described by ultra-soft pseudopotentials from the Quantum Espresso database. The wave functions and the charge density were expanded in plane waves with 50 and 500 Ry cutoffs, respectively, in all cases, leading to a convergence of the total energy less than 1 mRy/atom. The electronic integration was performed by sampling the Brillouin zone with $N_1 \times N_2 \times N_3$ k -point grids according to the Monkhorst-Pack scheme (Monkhorst and Pack, 1976), with N_i dependence on the minerals (Table 1). The structures were optimized using variable cell shape molecular dynamics (Wentzcovitch, 1991), and the forces on atoms were minimized to less than 10^{-4} Ry/a.u..

Phonon frequencies were computed based on the linear response method (Baroni et al., 2001). They were derived from the second-order derivative of the total energy with respect to atomic displacements. Dynamical matrices were computed on a regular q mesh and then interpolated into a dense q mesh to obtain the vibrational density of state of the minerals. The sizes of the regular and dense q mesh also depend on the minerals (Table 1).

3. Results

3.1. Crystalline structure

Arsenopyrite has a monoclinic symmetry, and belongs to the space group $P12_1/c1$. The arsenopyrite structure is derivative of the marcasite structure (Hem et al., 2001), which may be viewed as chains of linked octahedra parallel to the c -axis (Mosselmans et al., 1995). In pyrite neighbouring octahedra share corners, while in marcasite and arsenopyrite each octahedron shares two edges (Wood and Strens, 1979). Gudmundite has the same structure as arsenopyrite. Our calculated structures of arsenopyrite and gudmundite are given in Table 2 together with experimental results. The structure parameters of pyrite-type disulphides were calculated using the

same functional and computational parameters as in our previous study (Liu et al., 2015), so we compare them with the present results in Tables 2, 3, and 4. In this group, each anion (S, As and Sb) has tetrahedral coordination to one anion and three cations (Fe). For pyrite, the bond lengths between the three cations (Fe) and one anion (S) are the same, but for arsenopyrite and gudmundite, the bond lengths are different. Thus, Table 2 lists the average bond lengths of Fe-S and Fe-As for arsenopyrite and the average bond lengths of Fe-S and Fe-Sb for gudmundite. For arsenopyrite, the GGA calculations underestimate the experimental lattice constants no more than 0.3%. For gudmundite, the calculated lattice constants a and c are 0.5% and 0.2% larger, respectively, than the measured lattice constants, and calculated lattice constant b is 0.2% smaller than the measured lattice constants. For these two minerals, the calculated interatomic distances and the angle β are also consistent with the available experiments. Thus, the calculated crystal structures of Fe sulphides based on GGA are in good agreement with experimental values (Bindi et al., 2012; Brostigen and Kjekshus, 1969; Buerger, 1939).

With pyrite-derivative structure and orthorhombic (pseudocubic) symmetry (Fleet and Burns, 1990), cobaltite belongs to the space group $Pca2_1$ (Giese et al. 1965) and the S-As dumbbells have ordered orientations (Makovicky, 2006), so the symmetries of these structures are lower than that of pyrite (Zoltai and Stout, 1984). With orthorhombic symmetry, costibite belongs to the space group $Pnm2_1$ (Cabri et al., 1970). The average bond lengths of Co-S and Co-As for cobaltite and the average bond lengths of Co-S and Co-Sb for costibite are listed in Table 3, together with experimental results and the crystal structure of cattierite. The calculated results are close to the experimental results (Andresen et al., 1967; Fleet and Burns, 1990; Rowland et al., 1975) and the errors are no more than 2.1%.

The structure of ullmannite can be derived by ordered substitution of Sb and S at the pyrite S sites, which globally gives rise to a lowering of the symmetry, with a change from the centrosymmetric $Pa\bar{3}$ space group (pyrite) to the acentric $P2_13$ group (ullmannite) (Carlini et al., 2012, 2013). Gersdorffite has the same structure as ullmannite. Both the calculated and the experimental structures of vaesite, gersdorffite and ullmannite are listed in Table 4. For gersdorffite and ullmannite, our calculated lattice constants overestimate the experimental lattice constants by no more than 0.4%. The calculated interatomic distances are also consistent with the available experiments (Foecker and Jeitschko, 2001; Nowack et al., 1991).

3.2. Vibrational properties

For pyrite, the calculated harmonic phonon frequencies from our previous study (Liu et al., 2015) are in good agreement with the experimental and previously calculated results (Blanchard et al., 2009; Bhrer et al., 1993; Spagnoli et al., 2010). For vaesite, the only existing measured data that can be compared with our calculated data are the Raman active modes. The five Raman active vibrational modes can be classified into the following symmetry species:

$$\Gamma^R(\text{NiS}_2) = A_g + E_g + 3T_g \quad (4)$$

The A_g , E_g , $T_g(1)$, $T_g(2)$ and $T_g(3)$ modes calculated by us are at 426, 282, 257, 285 and 431 cm^{-1} , respectively, while the experimental A_g , E_g , $T_g(1)$ and $T_g(3)$ modes measured by Bishop et al. (2000) are 414, 274, 263 and 468 cm^{-1} , respectively. Their experimental results lack the $T_g(2)$ mode.

The irreducible representations of arsenopyrite can be given as follows:

$$\Gamma(\text{FeAsS}) = 9A_g + 9B_g + 9A_u + 9B_u \quad (5)$$

Here, the A_g and B_g modes are Raman active and the A_u and B_u modes are IR-active. For

arsenopyrite, complete experimental data of the Raman and infrared-active modes do not exist. In the infrared spectra, only three wavenumber modes at 274, 368, and 435 cm^{-1} , measured by Lutz et al. (1983), can be compared with our calculated results at 270, 353 and 433 cm^{-1} . In the Raman spectra, the five wavenumber modes at 198, 313, 337, 404 and 412 cm^{-1} measured by Giudici et al. (2007) can be compared with our calculated data at 200, 321, 332, 399 and 402 cm^{-1} . For other sulphides, sulpharsenides and sulphantimonides of Fe, Co and Ni, there seems to be few corresponding measured vibration frequency data. The calculated frequencies by PBE approximation generally underestimate the measured Raman and infrared frequencies by a few percent, and this deviation is expected to lead to a systematic error in the reduced partition function ratio (β -factor). By comparing the calculated frequencies with the experimental ones, a scaling factor is often used to multiply the theoretical frequencies to minimize this type of error. Because of the lack of experimental frequency data, it is impossible to estimate analogous scaling factors of minerals, and using scaling factors may also lead to uncertainties. Therefore, we do not use the scaling factor for frequency correction in the present study.

The PBE approximation has been used to calculate isotope fractionation in some studies (Blanchard et al, 2009; Liu et al., 2014, 2015; Méheut et al., 2009, 2010; Méheut and Schauble, 2014; Schauble, 2011) and has been shown to be a good exchange correlation functional for isotope fractionation. Our calculated crystal structures and vibrational frequencies agree well with experimental data for these sulphide minerals, which also indicates that the PBE approximation can be used to calculate S isotope fractionation in these sulphide minerals.

3.3. β -factors

In this study, the reduced partition function ratios of $^{34}\text{S}/^{32}\text{S}$ ($10^3 \ln \beta_{34-32}$) are calculated in

the range of 0-1000 °C. The calculated data are fitted to a least-squares polynomial, and a second-order polynomial is sufficient to accurately fit the data over the temperature range. The fitting parameters are listed in Table 5, and $10^3 \ln \beta_{34-32}$ as a function of temperature are shown in Fig. 1. As shown in Fig. 1, $^{34}\text{S}/^{32}\text{S}$ ($10^3 \ln \beta_{34-32}$) decreases in the order of arsenopyrite > pyrite > cobaltite > gudmundite > cattierite > costibite > vaesite > gersdorffite > ullmannite. For the sulphides with the same cation, the order of ^{34}S enrichment is arsenopyrite > pyrite > gudmundite in Fe sulphides, cobaltite > cattierite > costibite in Co sulphides, and vaesite > gersdorffite > ullmannite in Ni sulphides. For the sulphides with the same anion pair, the order of ^{34}S enrichment is pyrite > cattierite > vaesite in disulphides, arsenopyrite > cobaltite > gersdorffite in sulpharsenides, and gudmundite > costibite > ullmannite in sulphantimonides.

4. Discussion

Various chemical properties can affect the magnitude of isotope fractionation. Heavy isotopes are preferentially concentrated in substances with greater bond stiffness (Bigeleisen and Mayer, 1947). The properties controlling bond stiffness are bond length, coordination number, oxidation state, electronegativity, etc. (Schauble et al., 2001; Schauble, 2004).

The relationship between bond length and isotope fractionation has been discussed for many stable isotopes such as Li, Mg, Si, Ca, Cr, Fe, and Ge isotopes (e.g., Feng et al., 2014; Hill and Schauble, 2008; Huang et al., 2014; Li et al., 2009; Schauble et al., 2004; Wunder et al., 2011; Young et al., 2009). In general, a shorter bond has stronger bond strength and higher vibrational energy, thus when at equilibrium, it is more enriched in heavy isotopes than a longer bond (Urey, 1947). However, it is difficult to understand the relationship between chemical bonding and S isotope fractionation in sulphide minerals. The structures of the sulphides are quite complex

because of the bonding characteristics (Zoltai and Stout, 1984). Most of the bonding in the sulphide minerals is covalent or metallic or both (Berry et al., 1983; Zoltai and Stout, 1984); the nature of the bonding has long been controversial (Antonov et al., 2009; Birkholz and Rudert, 2008; Brostigen and Kjekshus, 1970; Cervantes et al., 2002; Finklea et al., 1976; Hulliger and Mooser, 1965; Pauling, 1978; Pauling and Huggins, 1934; Schmøkel et al., 2014; Sithole et al., 2003; Sourisseau et al., 1991). In disulphides, sulpharsenides and sulphantimonides, not only can the S atom form metal-sulphur bonding with the metal atom, but it can also form metalloid-sulphur bonding with the metalloid atom (e.g., S, As and Sb atoms). Thus, the effects of both the metal-sulphur bond-length and the metalloid-sulphur bond-length on S isotope fractionation must be taken into account.

Heavy isotopes tend to be concentrated in substances with low coordination number (Schauble, 2004). For sulphur-bearing systems, the effect of the oxidation state of S on isotope fractionation is especially important; higher oxidation states of S are enriched in the heavy isotopes relative to lower oxidation states (Bachinski, 1969; Sakai, 1968). The coordination numbers of S in these sulphides are the same, and the oxidation state of S is uniform at -2. Thus, it seems that the effects of S coordination number and oxidation state on S isotope fractionation properties of these sulphide minerals make no difference.

4.1. Influence of metal substitution on equilibrium S isotope fractionation

The relationship between the average metal-sulphur bond lengths and calculated reduced partition function ratios of $^{34}\text{S}/^{32}\text{S}$ (β_{34-32}) is shown in Fig. 2. The β_{34-32} values decrease with increasing average metal-sulphur bond lengths in the sulphides with the same anion pair. There seems to be a linear dependence between metal-sulphur bond lengths and β_{34-32} , which implies S

isotope fractionations in these minerals are determined by the metal-sulphur bond strength to some extent. Thus, S isotopes can be fractionated between minerals with identical anions if their metal-sulphur bond lengths are different.

Figure 3 illustrates the relationship between the average metalloid-sulphur bond lengths and calculated β_{34-32} values of these sulphides. The average metalloid-sulphur bond lengths do not appear to be sensitive to the substitution of cations. For sulpharsenides, the As-S bond lengths in CoAsS and NiAsS are almost the same, but their β_{34-32} values are very different. Similarly for sulphantimonides, the Sb-S bond lengths in CoSbS and NiSbS are almost the same, but their β_{34-32} values are very different. This suggests that S isotope fractionation in the sulphides with the same anion pair is not controlled by the metalloid-sulphur bond lengths.

For the studied sulphide minerals, each S atom has bonds with three metal atoms and another metalloid atom. The relationship between the average bond lengths of three metal-sulphur bonds and one metalloid-sulphur bond and the β_{34-32} values is shown in Fig. 4. As illustrated in Fig. 4, the average bond lengths of three metal-sulphur bonds and one metalloid-sulphur bond is linearly correlated with S isotope fractionation factors in the sulphides with the same anion pair. It seems that the correlation between β_{34-32} values and average bond lengths of three metal-sulphur bonds and one metalloid-sulphur bond is much better than that between β_{34-32} values and average metal-sulphur bond lengths. Therefore, by comparing Figs. 2, 3 and 4 for the sulphides with the same anion pair, metal-sulphur bond strength dominantly controls S isotope fractionation properties, and metalloid-sulphur bond strength also plays a role in changing the isotope fractionation properties.

A common structural feature of these sulphide minerals is that each anion (S, As, and Sb) is

tetrahedrally bonded to another anion plus three cations. Schauble (2011) found an overall correlation between $^{26}\text{Mg}/^{24}\text{Mg}$ with model volumes of Mg-O coordination polyhedra. We also calculated the volumes of S coordination tetrahedrons in these sulphides, and the relationship between the volumes of tetrahedrons and the calculated β_{34-32} values is illustrated in Fig. 5. For these sulphides with the same anion pair, negative correlations are observed between β_{34-32} values and the volumes of tetrahedrons.

Electronegativity, originally defined by Pauling (1960), is a measure of the power of an atom in a molecule to attract electrons. Electronegativity also has an effect on isotope fractionation, and strong correlations are observed between equilibrium fractionation factors and electronegativity for equilibrium isotope fractionation of Fe, Ni, Cu, Zn and Si (Fujii et al., 2014; Méheut and Schauble, 2014). The effect of cation X on Si isotope fractionation in silicate minerals will increase with decreasing electronegativity of X (Méheut and Schauble, 2014). The $\ln \beta$ values for Fe, Ni, Cu, and Zn bound to a number of inorganic and organic ligands increase with increasing group electronegativity of the ligands (Fujii et al., 2014). The Pauling electronegativity of metal elements increases in the order of Fe ($\chi(\text{Fe})=1.83$) < Co ($\chi(\text{Co})=1.88$) < Ni ($\chi(\text{Ni})=1.92$), contrary to the order of ^{34}S enrichment $\text{FeS}_2 > \text{CoS}_2 > \text{NiS}_2$ in disulphides, $\text{FeAsS} > \text{CoAsS} > \text{NiAsS}$ in sulpharsenides, and $\text{FeSbS} > \text{CoSbS} > \text{NiSbS}$ in sulphantimonides. It seems clear that the order of heavy isotope enrichment in the sulphides with the same anion pair has some relation to the electronegativity of cations and that the $^{34}\text{S}/^{32}\text{S}$ ratios decrease with increasing electronegativity of cations.

4.2. Influence of metalloid substitution on equilibrium S isotope fractionation

In pyrite-group sulphides, the substitution of a metalloid element for S may cause changes in

the mineral structures, as well as bonding environment. For example, the symmetry of Fe sulphides changes from the centrosymmetric $Pa\bar{3}$ space group (FeS_2) to the monoclinic symmetric $P12_1/c1$ space group (FeAsS and FeSbS) during As-S substitution and Sb-S substitution. For different sulphides (Fe sulphides, Co sulphides and Ni sulphides), the extent of structural change arising from metalloid substitution is different. Not only metalloid-sulphur bond lengths but also metal-sulphur bond lengths are responsive to metalloid substitution. However, for most of the sulphides studied in the present paper, the effect of metalloid substitution on S isotope fractionation is much smaller than that of metal substitution. For example, the largest S isotope fractionation factor ($10^3 \ln \alpha$) arising from metalloid substitution is 4.16‰ between CoAsS and CoSbS at 25 °C, which is smaller than most of the S isotope fractionation factors between the sulphides arising from metal substitution at 25 °C (e.g., $10^3 \ln \alpha_{\text{FeAsS-NiAsS}} = 7.76\text{‰}$, $10^3 \ln \alpha_{\text{FeS}_2\text{-NiS}_2} = 6.53\text{‰}$, $10^3 \ln \alpha_{\text{FeSbS-NiSbS}} = 6.79\text{‰}$, $10^3 \ln \alpha_{\text{FeS}_2\text{-CoS}_2} = 5.06\text{‰}$, $10^3 \ln \alpha_{\text{CoAsS-NiAsS}} = 5.16\text{‰}$).

As shown in Fig. 2, metalloid substitution can generate different observable changes in the average metal-sulphur bond lengths. For Co sulphides, the average metal-sulphur bond lengths are linearly correlated with β_{34-32} values, but for Fe and Ni sulphides there is not a strong correlation between $^{34}\text{S}/^{32}\text{S}$ and average metal-sulphur bond lengths. From Fig. 2 and Fig. 3, it is observed that the changes of average metalloid-sulphur bond lengths caused by metalloid substitution are greater than that of the average metal-sulphur bond lengths. As illustrated in Fig. 3, there does not appear to be a strong correlation between β_{34-32} values and average metalloid-sulphur bond lengths in Fe sulphides and Co sulphides. Furthermore, in both Fe sulphides and Co sulphides, the average bond lengths of three metal-sulphur bonds and one metalloid-sulphur bond are also poorly

correlated with calculated β_{34-32} values (Fig. 4). As shown in Fig. 5, there is a linear correlation between β_{34-32} values and the volumes of sulphur coordination tetrahedrons in Ni sulphides, but correlations between β_{34-32} values and volumes of sulphur coordination tetrahedrons in Fe sulphides and Co sulphides are non-existent. It seems that S isotope fractionation is dominantly controlled by metal-sulphur bond strength and metalloid-sulphur bond strength in Co sulphides and Ni sulphides, respectively. This suggests that the isotope fractionation effects from metalloid substitution are very complex, and further research is needed.

4.3. Implications

Our calculations suggest that the effect of metal substitution on the S isotope fractionation properties of these sulphides is large and that the metal-sulphur bond lengths are sensitive to the metal substitution. At a given temperature, S isotope fractionation arising from metal substitution is significantly large, and the larger the difference between the average metal-sulphur bond lengths, the more significant the S isotope fractionation. For example, the smallest S isotope fractionation factor ($10^3 \ln \alpha$) arising from metal substitution is approximately 1.47‰ between CoS_2 and NiS_2 at 25 °C and decreases to 0.22‰ at 500 °C; the largest S isotope fractionation factor ($10^3 \ln \alpha$) arising from metal substitution is approximately 7.76‰ between FeAsS and NiAsS at 25 °C and decreases to 0.45‰ at 1000 °C. Thus, it is possible to use S isotope fractionation arising from metal substitution as an isotope geothermometer to estimate the temperature of formation and evolution of ore deposits. In fact, metal substitution in sulphides is very common in nature. For example, the (Fe,Co,Ni)-sulpharsenides exhibit large variations in Fe, Co and Ni contents (Hem et al., 2001), and these minerals are commonly found coexisting in hydrothermal deposits (Yang and Downs, 2008); members of the $(\text{Cu}, \text{Fe})\text{S}_2$ solid solution crystallize in the pyrite structure with

Cu and Fe being statistically distributed on the metal sites (Schmid-Beurmann and Lottermoser, 1993); bravoite, with variable substitution of Ni for Fe within pyrite, has been found in many places (Bayliss, 1989); Cd is hosted mainly in sphalerite as isomorphic impurities (Lin and Tiegeng, 2001). Therefore, S isotope fractionation between sulphides with different metal contents and S isotope fractionation arising from isomorphic replacement of metal elements could provide useful thermometers with wider applications. More theoretical and experimental studies are needed to fully establish similar thermometers in the future.

Although the effect of metalloid substitution on S isotope fractionation is generally much smaller than that of metal substitution, S isotope fractionation arising from metalloid substitution may be useful. For example, $10^3 \ln \alpha_{\text{CoAsS-CoSbS}}$, $10^3 \ln \alpha_{\text{FeAsS-FeSbS}}$ and $10^3 \ln \alpha_{\text{NiS}_2\text{-NiSbS}}$ decrease from 4.16‰ to 0.36‰, 2.96‰ to 0.23‰, and 2.60‰ to 0.23‰, respectively, with temperature increasing from 25 °C to 800 °C. Metalloid substitution in sulphides is also very common in nature; for example, in CoAsS, As and S may partially substitute for each other (Bayliss, 1969; Hem, 2006; Petruk et al., 1971), and Fuess et al. (1987) found partially mixed S and As populations in FeAsS. Therefore, it is possible to use S isotope fractionation arising from metalloid substitution as an isotope geothermometer of geological processes. Our results suggest that there is no clear relevance between bond-length changes and isotope fractionations arising from metalloid substitution. For example, the metalloid-sulphur bond-length change is 0.436 Å with substitution of Sb for S in Co sulphides, which is larger than that (0.250 Å) with substitution of Sb for As in Co sulphides, while $10^3 \ln \alpha_{\text{CoS}_2\text{-CoSbS}}$ (1.08‰) is smaller than $10^3 \ln \alpha_{\text{CoAsS-CoSbS}}$ (4.16‰) at 25 °C; the metal-sulphur bond-length change is 0.054 Å with substitution of As for S in Fe sulphides, which is larger than that (0.021 Å) with substitution of S

for Sb in Fe sulphides, while $10^3 \ln \alpha_{\text{FeAsS-FeS}_2}$ (0.63‰) is smaller than $10^3 \ln \alpha_{\text{FeS}_2\text{-FeSbS}}$ (2.33‰) at 25 °C. These results may provide hints for the studies of other stable isotopic systems of minerals in which the isotope fractionations are small but the crystal structure differences are large.

5. Conclusion

In the present paper, the reduced partition function ratios of $^{34}\text{S}/^{32}\text{S}$ for Fe, Co and Ni sulpharsenides and sulphantimonides over the temperature range of 0 to 1000 °C were calculated using first-principles calculations. The order of ^{34}S enrichment in these minerals is arsenopyrite > cobaltite > gudmundite > costibite > gersdorffite > ullmannite. Sulphur isotope fractionation caused by metal substitution is dominantly controlled by the metal-sulphur bond strength, and the electronegativity of cations also plays an important role in controlling the fractionation. Metalloid substitution can also generate some effect on the metalloid-sulphur bond lengths, metal-sulphur bond lengths, and isotope fractionation factors, but there is no clear relevance between bond-length changes and isotope fractionations arising from metalloid substitution. Additionally, the effect of metalloid substitution on S isotope fractionation is generally much smaller than that of metal substitution. Sulphur isotope fractionations arising from metal substitution and metalloid substitution may be a useful tool for estimating the temperature of formation and evolution of ore deposits.

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Figure captions

Fig. 1. The temperature dependence of the equilibrium reduced partition function ratios of $^{34}\text{S}/^{32}\text{S}$ ($10^3 \ln \beta_{34-32}$) for sulphide minerals.

Fig. 2. $^{34}\text{S}/^{32}\text{S}$ fractionation factors at 25 °C vs. average metal-sulphur bond lengths.

Fig. 3. $^{34}\text{S}/^{32}\text{S}$ fractionation factors at 25 °C vs. average metalloid-sulphur bond lengths.

Fig. 4. $^{34}\text{S}/^{32}\text{S}$ fractionation factors at 25 °C vs. average bond lengths of three metal-sulphur bonds and one metalloid-sulphur bond.

Fig. 5. $^{34}\text{S}/^{32}\text{S}$ fractionation factors at 25 °C vs. volumes of sulphur coordination tetrahedron.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Table 1. K mesh used for Brillouin zone summations over electronic states, regular q mesh used for real space force constant matrix, and dense q mesh used for the reduced partitions function ratio.

Mineral	K mesh	Regular q mesh	Dense q mesh
Arsenopyrite	4×4×4	2×2×2	8×8×8
Gudmundite	4×4×4	2×2×2	8×8×8
Cobaltite	4×4×4	2×2×2	8×8×8
Costibite	6×6×8	3×3×4	9×9×12
Gersdorffite	4×4×4	4×4×4	12×12×12
Ullmannite	4×4×4	4×4×4	12×12×12

Table 2 Comparison of the calculated and experimental structures of pyrite, arsenopyrite and gudmundite

FeS ₂	Calculated ^a	Experimental ^b	Error(%)
a(Å)	5.405	5.418	-0.2
V(Å ³)	157.902	159.044	-0.7
Fe-S (Å)	2.255	2.262	-0.3
S-S (Å)	2.189	2.177	0.6
FeAsS	This study -GGA	Experimental ^c	Error(%)
a(Å)	5.7440	5.7612	-0.3
b(Å)	5.6776	5.6841	-0.1
c(Å)	5.7631	5.7674	-0.1
β	111.880	111.721	0.1
V(Å ³)	174.408	175.456	-0.6
Fe-S (Å)	2.2013	2.2306	-1.3
As-S (Å)	2.4134	2.3743	1.7
Fe-As (Å)	2.4084	2.3973	0.5
FeSbS	This study -GGA	Experimental ^d	Error(%)
a(Å)	6.0506	6.02	0.5
b(Å)	5.9192	5.93	-0.2
c(Å)	6.0319	6.02	0.2
β	67.418	67.87	-0.7
V(Å ³)	199.468	199.074	0.2
Fe-S (Å)	2.2345	2.2337	0.0
Sb-S (Å)	2.6168	2.6138	0.1
Fe-Sb (Å)	2.5696	2.5664	0.1

a Liu et al., 2015; b Brostigen and Kjekshus, 1969; c Bindi et al., 2012; d Buerger, 1939.

Table 3 Comparison of the calculated and experimental structures of cattierite, cobaltite and costibite

CoS ₂	Calculated ^a	Experimental ^b	Error(%)
a(Å)	5.506	5.528	-0.4
V(Å ³)	166.920	168.929	-1.2
Co-S (Å)	2.307	2.319	-0.5
S-S (Å)	2.138	2.126	0.6
CoAsS	This study -GGA	Experimental ^c	Error(%)
a(Å)	5.5909	5.5833	0.1
b(Å)	5.5951	5.5892	0.1
c(Å)	5.5847	5.5812	0.1
V(Å ³)	174.699	174.168	0.3
Co-S (Å)	2.2818	2.2935	-0.5
As-S (Å)	2.3245	2.2924	1.4
Co-As (Å)	2.3727	2.3615	0.5
CoSbS	This study -GGA	Experimental ^d	Error(%)
a(Å)	4.844	4.873	-0.6
b(Å)	5.833	5.852	-0.3
c(Å)	3.650	3.608	1.2
V(Å ³)	103.131	102.889	0.2
Co-S (Å)	2.325	2.337	-0.5
Sb-S (Å)	2.574	2.521	2.1
Co-Sb (Å)	2.495	2.494	0.0

a Liu et al., 2015; b Andresen et al., 1967; c Fleet and Burns, 1990; d Rowland et al., 1975.

Table 4 Comparison of the calculated and experimental structures of vaesite, gersdorffite and ullmannite

NiS ₂	Calculated ^a	Experimental ^b	Error(%)
a(Å)	5.613	5.6765	-1.1
V(Å ³)	176.842	182.912	-3.3
Ni-S (Å)	2.365	2.394	-1.2
S-S (Å)	2.073	2.074	-0.0
NiAsS	This study -GGA	Experimental ^c	Error(%)
a(Å)	5.7126	5.6888	0.4
V(Å ³)	186.424	184.103	1.3
Ni-S (Å)	2.3487	2.3485	0.0
As-S (Å)	2.3311	2.2988	1.4
Ni-As (Å)	2.4166	2.4007	0.7
NiSbS	This study -GGA	Experimental ^d	Error(%)
a(Å)	5.9493	5.9341	0.3
V(Å ³)	210.571	208.961	0.8
Ni-S (Å)	2.3762	2.3757	0.0
Sb-S (Å)	2.5625	2.5239	1.5
Ni-Sb (Å)	2.5704	2.5628	0.3

a Liu et al., 2015; b Nowack et al., 1991; c Foecker and Jeitschko, 2001; d Foecker and Jeitschko, 2001

Table 5 Calculated reduced partition function ratios ($10^3 \ln \beta_{34-32}$) for sulphide minerals

Mineral	Chemical formula	<i>a</i>	<i>b</i>	<i>c</i>
Pyrite	FeS ₂	0.00777	1.77024	-0.00748
Arsenopyrite	FeAsS	0.00164	1.82574	-0.00741
Gudmundite	FeSbS	0.01065	1.54534	-0.00596
Cattierite	CoS ₂	0.00337	1.28330	-0.00412
Cobaltite	CoAsS	0.03581	1.56302	-0.00486
Costibite	CoSbS	0.01699	1.17158	-0.00282
Vaesite	NiS ₂	0.01057	1.14580	-0.00359
Gersdorffite	NiAsS	-0.00293	1.09399	-0.00362
Ullmannite	NiSbS	-0.00245	0.89896	-0.00208

$10^3 \ln \beta = a + bx + cx^2$, where $x = 10^6 / T^2$. *T* is temperature in Kelvin.