Molecular Scale Studies that Inform Trace Element Sulfide Evaporation and Atomization Behavior During Coal Combustion

Anastasia A. Artemyeva^a, Wayne S. Seames^b, David T. Pierce^a and Evguenii I. Kozliak^{a}*

^a University of North Dakota, SUNRISE Group; Department of Chemistry, 151 Cornell St. Stop 9024, Grand Forks, ND 58202, U.S.A.

^b University of North Dakota, SUNRISE Group; Department of Chemical Engineering, 241 Centennial Dr. Stop 7101, Grand Forks, ND 58202, U.S.A.

* Corresponding Author: voice: +1 701-777-2145, fax: +1 701-777-2331,
email: evguenii.kozliak@und.edu.

ABSTRACT

Understanding the chemical mechanisms of trace element (TE) evolution is essential for accurate modeling of coal combustion. A novel graphite furnace atomic absorption spectrometry (GFAAS) method was used to simulate the evaporation and atomization behavior of TE sulfides (arsenic, antimony and selenium) in the two distinct microenvironments that mineral inclusions and exclusions experience during the onset of coal combustion. Additional insights were obtained using thermogravimetric analysis-differential scanning calorimetry (TGA-DSC). Potassium polysulfide was used as an additive to water to facilitate the dissolution of all three TE sulfides. TE sulfides in inclusions were studied by adding the test mixture to a graphite tube in a reducing (anaerobic) micro-environment whereas the TE evolution in excluded sulfide minerals was studied by blocking the graphite tube surface with an inert ZrO_2 or WO_3 coating. Arsenic sulfide, As_2S_3 , exhibits a lower Arrhenius activation energy of atomization, E_a , than that of the corresponding oxide in both mineral inclusions and exclusions, apparently because of the availability of a specific facile path to atomization. A higher E_a was observed for antimony sulfide, Sb_2S_3 , than that of the corresponding oxide from inclusions and is most likely due to its strong binding affinity to the carbon tube surface. The low GFAAS signal of selenium sulfide suggests the formation of molecular clusters, e.g., Se_2 , Se_8 or similar mixed clusters with sulfur atoms prior to vaporization, an effect not observed for selenium oxide evaporation. For all three

TE sulfides, either elemental species or unstable sulfides with low sulfur content appear to be predominant in the gas phase associated with both mineral inclusions and exclusions, with TE sulfide evaporation being the rate limiting step. Comparing the GFAAS activation energy values obtained with and without the coating showed that in a reducing micro-environment (anaerobic conditions) characteristic during the initial period of combustion for mineral inclusions, carbon merely adsorbs TE sulfides without chemical reactions. Yet TGA-DSC data showed that powdered graphite may react with TE sulfides in an oxidizing micro-environment (microaerobic conditions), such as those experienced during the later period of combustion for inclusions and during the entire combustion period for exclusions thus accelerating TE evolution without making qualitative changes in the vapor composition.

Keywords: trace element partitioning; sulfide/pyrite fraction; mineral inclusions; excluded minerals; coal combustion; graphite furnace atomic absorption spectrometry.

Abbreviations:

TEs – trace elements

CAAAAs – Clean Air Act Amendments

GFAAS – graphite furnace atomic absorption spectrometer

TGA – thermogravimetry

DSC – differential scanning calorimetry

1. Introduction

An important environmental issue associated with coal combustion is the release of trace elements (TEs) into the atmosphere. The U.S. Clean Air Act Amendments (CAAAAs) classify these TE species as toxic air pollutants [1]. Both the form of TE occurrence and the coal type determine the TE solid/gas phase partitioning within the combustion system which ultimately affects their environmental fate and the toxic effects that may ensue. Understanding the mechanisms of TE partitioning during coal combustion is an essential step towards minimizing the environmental impact caused by the emission of TEs from the substantial installed capacity of coal-fired power generation systems throughout the world.

TEs occur in coal in three different forms: organically associated, mineral inclusions and excluded minerals, characterized by a decreasing access to carbon and decreasing peak localized temperature within this series. The organically associated TEs exhibit strong interactions with the coal carbon matrix whereas TEs within mineral exclusions are too remote from the carbon for significant interaction. TEs in mineral inclusions are surrounded by the carbon matrix, which may interact with the TEs as included minerals begin to melt [2, 3]. The distance from the combusting coal matrix also affects the localized temperature, which could vary as much as 100-1,000K, as well as the presence or absence of available oxygen in the microenvironment the TE will experience.

A pronounced difference in both localized temperature and oxygen availability is expected to significantly affect partitioning and speciation as TEs transition into the gas phase. This difference in TE partitioning and speciation may also be amplified by more subtle yet no less significant specific effects of the chemical microenvironment surrounding the TE atoms such as the TE's chemical speciation in the solid phase and the interactions of TE-containing molecules with the adjacent inorganic matrix. While temperature changes and oxygen depletion can be taken into account by modelling, the presumed impacts of chemical microenvironments can neither be modeled using the currently employed methods [4-7] nor studied *in situ* with real coal particles. This consideration warrants conducting experimental studies using simulated environments.

This point is worth emphasizing. It is not possible with current techniques to study the distinctly different microenvironments of mineral inclusions and exclusions using real coal particles. The best that can currently be accomplished is the study of the surrounding microenvironment or of the overall behavior of TEs from coal particles, irrespective of originating domain (e.g. inclusion, exclusion, or organically associated). Yet it is the highly dynamic, very short lived initial stages of combustion that influence TE partitioning the greatest. Accurate modeling of TE behavior requires greater insight into the mechanisms of TE partitioning than can be achieved with current coal study methods. As such, simulated environments must be employed.

In our previous work, a method was developed that simulates and evaluates the partitioning of organically associated TEs. The original method allows for the measurement of the kinetic parameters associated with TE vaporization/atomization in an environment that corresponds to

the behavior expected from TEs in the organic fraction of a coal particle. It is based on the use of a modified graphite furnace atomic absorption spectrometer (GFAAS) as both an *in situ* measurement platform and carbon source [8]. The method was then extended to study TE partitioning from coal mineral inclusions by introducing homogeneously mixed TE/inorganic matrix solutions into the graphite furnace tube [9] and to simulate TE partitioning from excluded minerals by introducing TEs, with or without matrices, into a metal oxide-coated graphite furnace tube [10] (i.e., in an environment where the TEs are not directly exposed to the carbon matrix).

However, the previous studies were only conducted with TE oxides. Completely absent were studies of the other equally important form for TEs in coal, namely TE sulfides. These TE sulfides are often associated with other sulfides in coal, e.g., pyrite, marcasite, galena, sphalerite, etc. [11] with pyrite association generally being the most common form. Thus, the goal of the current study was to apply the previously developed method to evaluate the release of TE sulfides from the pyrite fraction of coal inclusions and exclusions.

The main challenge in this work was developing a method to introduce representative samples of TE sulfide, with and without matrices, into the GFAAS as homogeneous mixtures, i.e., solutions. While As(III), Sb(III), and Se(IV) oxides are soluble in water, the corresponding TE sulfides are not. However, we were able to dissolve all three TE sulfides in water upon the addition of sulfide and polysulfide ions, which are essential components of all sulfide mineral inclusions and exclusions in coal. This finding laid the foundation for this study allowing the trends in TE sulfide atomization with and without accessible carbon to be investigated.

It should be noted that coal contains numerous other entities, such as volatile matter and metal oxides, that may impact TE partitioning behavior. The impacts of these other entities is outside of the scope of the present study but will be investigated in future work. Furthermore, untreated coal-derived flue gas is known to be a complex mixture containing numerous species such as particulates, nitrogen, carbon dioxide, moisture, oxygen, sulfur dioxide, sulfur trioxide, nitrogen oxides and hydrogen chloride [12-15]. These gas-phase species may also impact TE partitioning behavior as well as post-volatilization secondary reactions. The impacts from these species was also outside of the scope of the current study

Just as for TE oxides [8], a complementary method based on thermogravimetry (TGA) coupled with differential scanning calorimetry (DSC) was used to decouple the TE vaporization

and atomization phenomena. The flow of nitrogen was varied between 400 and 50 mL/min during TGA experiments to allow simulation of both near-anaerobic (reducing micro-environment) and microaerobic conditions (oxidizing micro-environment).

These two conditions, near-anaerobic and microaerobic, are important for accurate modeling of trace element partitioning. Included material is completely surrounded by a coal matrix. During the initial stages of combustion, oxidation of the coal leads to a highly reducing environment for the inclusions. As combustion progresses, carbon oxidation slows and the microenvironment surrounding the inclusion goes to neutral and then finally to an oxidizing condition. These rapidly changing conditions can only be studied using model systems such as those devised here.

Similarly, the microenvironment surrounding mineral exclusions will be at a lower oxygen content than the surrounding bulk flue gas, but is likely to never reach reducing conditions. Thus an oxidizing micro-environment is likely to replicate that of exclusions during the initial stages of combustion [16]. In this work, we postulated that the use of TGA-DSC under varied flow rates may provide a bridge to GFAAS data obtained under strictly anaerobic (reducing) conditions. As a result, the obtained data, though qualitative and indirect, provided novel and somewhat unexpected information on the influence of traces of oxygen on TE sulfide evolution in the presence of elemental carbon.

2. Experimental Section

2.1. Materials and reagents.

Potassium polysulfide (Acros Organics, New Jersey, USA) was used to prepare 11 mg/mL matrix solutions. As_2S_3 (diarsenic trisulfide henceforth called arsenic sulfide, Strem Chemicals, Newburyport, MA, USA), Sb_2S_3 (diantimony trisulfide henceforth called antimony sulfide, Strem Chemicals, Newburyport, MA, USA) and SeS_2 (selenium disulfide henceforth called selenium sulfide, Alfa Aesar, Ward Hill, MA, USA) were used to prepare 100 ppm aqueous stock solutions of TE sulfides in their most stable oxidation state. Standard 100 ppm stock solutions of TE sulfides in 11 mg/mL K_2S_n ($n=2-6$) were diluted with water 100-fold to obtain a 1.0 ppm TE sulfide concentration in 0.11 mg/mL potassium polysulfide. 0 – 400 ppb solutions of TE sulfides for sulfide matrix simulating experiments were then prepared by dilution of 1.0 ppm solutions with 0.11 mg/mL K_2S_n . All solutions were stored in a refrigerator at 4 °C. Water

deionized to an 18 MOhm·cm resistivity (Millipore, Billerica, MA, USA; model Direct-Q® 3) was used for all dilutions.

The 0.11 mg/mL polysulfide matrix concentration (0.001M with respect to potassium sulfide) was selected to assure TE sulfide dissolution while keeping the reference signal below 1.0 AU to avoid artifacts in the target TE absorbance signal. The TE sulfide solutions in potassium polysulfide were introduced into either an uncoated graphite furnace tube or a tube that had been coated with a low-volatility metal oxide as described below.

An alternative way to dissolve SeS₂ was to use carbon disulfide as a solvent. SeS₂ was dissolved in CS₂ (Sigma Aldrich, St. Louis, MO, USA) to prepare a 100 ppm stock solution. 400-1200 ppb solutions of selenium sulfide were then prepared by dilution of the corresponding stock solution with carbon disulfide. Higher SeS₂ concentrations had to be used compared to potassium polysulfide solutions because of lower absorbance signals.

Zr (zirconia) coatings were prepared according to the injection procedure described by Laborda et al. [17]. A 0.05 M ZrOCl₂ solution was prepared using ZrOCl₂·8H₂O (MP Biomedicals, Solon, OH). 20.0 µL of this solution was injected into a graphite tube followed by a programmed heating cycle (Supplementary Table 1). The procedure was repeated three times. Before analysis, a coating activation procedure was conducted (Supplementary Table 2), which was shown earlier to improve the sensitivity of measurements [18].

Tungsten (VI) oxide coatings were prepared according to a procedure similar to that described above for zirconia coated tubes [19]. Na₂WO₄·2H₂O was used as the starting material (Acros Organics, New Jersey, USA) to prepare a 0.05 M Na₂WO₄ solution. The same temperature programs as those described for zirconia-coated tubes were used for the injection of tungsten oxide coating material and its activation (Supplementary Tables 1 and 2, respectively).

For TGA-DSC experiments, As₂S₃, Sb₂S₃ and SeS₂ were used. The sample size was 5 – 10 mg. When conducting experiments to study the influence of elemental carbon, the above-described standard compounds were mixed with activated carbon (Acros Organics, NJ, USA) in a 1:3 mass ratio. The sample size was 20 – 40 mg.

2.2. Instrumentation.

The primary simulated TE partitioning experiments were accomplished using a Z-2000 Zeeman Flame/Furnace Tandem Atomic Absorption Spectrometer (Hitachi High Technologies, Japan). Atomic and background absorbance (i.e., reference) signals were measured simultaneously. Pyrolytically coated cylindrical Pyro Graphite Tubes HR (7J0-8880) (Hitachi, Tokyo, Japan) were used, with a length of 29 mm and a diameter of 5 mm. The signals were recorded every 20 ms using the manufacturer provided software (Hitachi). The flow rate of argon (Ultra Pure Carrier Ar, Airgas, USA) in the GFAAS was set at 30 mL/min (the manufacture recommended flow rate). The independence of TE atomization activation energies from this parameter was demonstrated earlier [2]. All experiments were conducted in triplicate. TE sulfides dissolved in an appropriate solvent were deposited on the center of the graphite tube by automatically controlled injections using an autosampler.

The temperature programs used for the determination of As_2S_3 , Sb_2S_3 and SeS_2 are provided in Supplementary Table 3. For safety reasons we used a modified temperature program in the experiments with carbon disulfide (Supplementary Table 4).. Namely, the drying temperature was decreased to 60°C because the self-ignition temperature of CS_2 is as low as 90°C [20]. To assure fast solvent evaporation below the self-ignition temperature, the ramp and hold times were increased to a maximum (100 seconds) while also increasing the gas flow rate to its maximum, 200 mL/min, except for the atomization step.

The injection volume of carbon disulfide solutions was set to 5.0 μL to minimize the volume of flammable solvent, while in experiments with potassium polysulfide it was set to 20.0 μL . To enable a correct comparison, the absorbances of SeS_2 in the CS_2 solution were adjusted to match the injection volumes used with potassium polysulfide solutions.

A Modline 5 infrared (IR) thermometer (Model 52-3024 with 2B lens, IRCON, Niles, IL, USA) was positioned above the furnace to accurately monitor the graphite furnace tube temperature throughout its heating cycle. It provided a RS-485 digital output of manufacturer calibrated temperatures to a host computer. The measured temperatures were in a range of 750–3000 °C within a focal distance of 152–305 mm, and with a response of 6.6 ms to 60 s. The slight modification of the Hitachi Z-2000 GFAAS, which has been described earlier [8], provided a precise synchronization between the absorbance signal and temperature measurements.

TGA-DSC experiments were conducted using a combined TGA-DSC Q600 device (TA Instruments, New Castle, DE, USA) under a N₂ (Ultra High Purity N₂, Airgas, USA) atmosphere. Aerobic (oxidizing) and near-anaerobic (reducing) conditions were simulated by variation of nitrogen flow rate. To model oxidizing micro-environments, the nitrogen flow rate was set to 50 mL/min, which allowed partial oxygen diffusion to the sample. To create a reducing atmosphere, the oxygen diffusion was prevented using a much higher nitrogen flow rate, 400 mL/min. Samples were heated from 35 to 1200 °C with a heating rate of 20 °C/min.

2.3. Calculation of activation energies

TE GFAAS atomization activation energies were calculated following the method described by Smets [21]. First, we calculated the rate constants of atom formation as:

$$k_1 = \frac{n(t)}{\int_t^{\infty} n(t)dt} = \frac{A(t)}{\int_t^{\infty} A(t)dt} \quad (1)$$

where k_1 is the first-order rate constant, $n(t)$ is the number of target TE atoms at time t , and $A(t)$ is the absorbance value at time t .

$A(t)$ was then obtained from the absorbance vs. time profiles using the GFAAS Hitachi software. The integrated absorbance ($\int_t^{\infty} A(t)dt$) was calculated using OriginPro 8.6.

Only the portion of the absorbance vs. time curve with a positive slope (i.e., the atom formation part of the peak as opposed to its dissipation) was used for Arrhenius plots; namely, the portion of the curve between $10 \times \text{noise}$ to $0.9 \times A_{\text{max}}$.

Temperature vs. time data were acquired using the Modline 5 IR thermometer as described above. The absorbance data were converted into a logarithmic form to determine the activation energy values from the slope of $\ln k_1$ vs. $1/T$. We used a linear regression to determine the Arrhenius parameters, which is a common method for the calculation of GFAAS activation energies [8]. To verify these results, nonlinear regression analysis was applied to select values using the R freeware. The activation energies obtained by the two methods matched within the limits of statistical error. When two peaks were observed in the absorbance profiles instead of

one, the multiple peak fit function in Origin was used for peak deconvolution as detailed in our previous work [8].

For TGA data, the derivative method was used for activation energy calculations. This approach is also based on the Arrhenius equation and the assumption of a first order reaction [10]:

$$\frac{dm}{dt} = -Ae^{\frac{-E_a}{RT}} m \quad (2)$$

where m is the sample mass.

An alternative integral method yielded much narrower linear temperature ranges and was thus discarded. Equation (2) can be converted into a logarithmic form to determine the activation

energy values from the slope of the $\ln(-\frac{dm/dt}{m})$ vs. $1/T$ plot [22]:

$$\ln\left(-\frac{dm/dt}{m}\right) = \ln A - \frac{E_a}{RT} \quad (3).$$

3. Results and Discussion

3.1. TE sulfide homogeneous sample preparation and GFAAS data utilization

For accurate determination of atomization activation energies, the TE sulfides should be injected into the furnace in a homogeneous, i.e., dissolved form. However, when As_2S_3 , Sb_2S_3 and SeS_2 are dissolved in water up to their solubility limits, the concentrations are too low to achieve a measurable GFAAS signal. To address the low solubility of TE sulfides in water, the TEs were dissolved in an aqueous solution of potassium polysulfide to form thioselenite, thioarsenite, and thioantimonite ions. The essential details of this approach, e.g., a suitable range of K_2S_n concentration, are provided in the Experimental section. The aqueous solution of potassium polysulfide thus served as both the solvent and as a matrix.

As TE sulfides usually occur in coal in association with metal sulfides or pyrite minerals, the TE evolution and atomization from sulfide/pyrite mineral inclusions and exclusions was experimentally simulated by injecting the homogeneous TE sulfide solutions in the presence of sodium polysulfide into uncoated and inert metal oxide coated graphite furnaces (ZrO_2 -coated and WO_3 -coated tubes), respectively. These inert metal oxide coatings are known to eliminate or, at least, hinder the accessibility of the TEs to the carbon in the GFAAS tubes [23, 24].

The activation energies obtained are listed in Table 1 and are compared to the corresponding values for As and Se oxides as well as Sb chloride, all of which were reported in a previous study [10]. To further illustrate the differences between TE oxide and sulfide evolution, the GFAAS atom evolution temperature profiles are shown in Fig. 1; this comparison being used in mechanistic evaluations. Furthermore, the E_a values obtained were matched to the activation energy and reaction enthalpy values determined by TGA/DSC under similar conditions (Table 2) and, if applicable, those of pertinent chemical reactions, to determine the rate determining step. As a “rule of thumb”, low E_a values, less than 40 kcal/mol, indicate that TE sulfide evaporation rather than any subsequent chemical reactions is rate limiting.

An important issue when studying exclusions is avoiding artifacts resulting from potential specific interactions of the TE with the coating, which would artificially increase the TE retention in the solid phase and increase the atomization activation energy. Our approach to overcome this problem was to use two different coating materials, ZrO_2 and WO_3 . Higher E_a values for one of the coatings indicates possible artificial specific interactions. If this occurs, then

only the values obtained with the other, lower E_a value coating were used for mechanistic considerations, since any coating interactions can only result in a higher E_a value.

3.2. Arsenic sulfide partitioning and atomization using GFAAS

Inclusions (when carbon is readily accessible). For arsenic sulfide, a rather low atomization activation energy, E_a , was obtained (Table 1). This value also matches the volatilization activation energies and thermodynamic enthalpy values obtained by TGA-DSC (Table 2). The enthalpy of As_2S_3 sublimation reported in the literature, 21 ± 1 kcal/mol [25], was lower than the E_a listed in Table 1, but this difference can be explained by arsenic sulfide adsorption on carbon in the GFAAS, hindering volatilization. This result indicates that physical processes limit the rate of arsenic sulfide atomization which differs from the corresponding arsenic oxide where a much higher E_a , 60 ± 5 kcal/mol [10], suggests that gas-phase reactions of elemental arsenic formation are rate limiting.

Rate limiting step. The lower E_a observed for arsenic sulfide atomization suggests a specific facile path toward elemental arsenic, which leads to the essential low-enthalpy physical process, i.e., As_2S_3 sublimation combined with desorption, becoming the rate limiting step. The available thermochemical data corroborate the hypothesis of facile arsenic sulfide decomposition in the gas phase, as the As-O average double bond enthalpy significantly exceeds that of As-S, 115 vs. 90 kcal/mol, respectively [26]. Furthermore, consistent with an easier elemental arsenic formation, As_2S_3 absorption peaks appeared at lower temperatures than did the corresponding As_2O_3 peaks (Fig. 1a).

However, the absorbance signals were slightly smaller for diarsenic trisulfide compared to diarsenic trioxide (Fig. 1a). Since a portion of the elemental arsenic is generated as As_2 from the sulfide at a lower temperature, it would not possess enough energy to dissociate into the corresponding atomic species. As_2 decomposition was identified earlier to be the likely rate limiting step for As_2O_3 atomization [9, 10]. Kinetic control of gas phase sulfide decomposition appears to take place, i.e., not all arsenic is generated in its most stable form, a diatomic molecule. The low signal intensity obtained during these experiments may also be due to kinetic limitations associated with removing all three sulfur atoms. They may be removed one by one in several steps, with a significant likelihood that the last sulfur atom remains attached to arsenic

when the signal is measured, despite the high propensity to decomposition. A facile thermal decomposition of As_2S_3 to As_2S_2 was reported earlier [27].

Exclusions (when carbon is less accessible). Qualitatively, the GFAAS profile remained unaltered when the graphite tube was coated compared to the uncoated tube results (Fig. 2a compared to Fig. 1a). The quantitative influence of carbon on the difference between mineral inclusions and exclusions was investigated by comparing the E_a values with and without the tube coatings, as shown in Table 1. For arsenic sulfide, the E_a values with and without the WO_3 coating were similar. This observation corroborates our conclusions that the rate limiting step of arsenic atomization occurs in the gas phase and that the accessibility of elemental carbon as a powerful reducing agent is not a significant factor. By contrast, the E_a value increased significantly in zirconia-coated furnaces, perhaps reflecting a strong specific adsorption of either As_2S_3 or its atomization intermediates on this material. This highlights the importance of using multiple coatings to insure that the results are reflective of the underlying chemistry and not artifacts of the experiments.

3.3. Antimony sulfide partitioning and atomization using GFAAS

Inclusions. In contrast to arsenic, the atomization activation energy turned out to be greater for Sb_2S_3 (51 ± 6 kcal/mol) compared to the corresponding chloride (38 ± 3 kcal/mol) [9], thus indicating that either the sulfide volatilization from the melt on the carbon surface or the subsequent antimony atomization from the sulfide may be hindered. If the latter is true, the high E_a value may indicate that the rate limiting step is a chemical reaction rather than the physical volatilization of antimony sulfide, for which the E_a value is known to be substantially lower, 32 kcal/mol [16, 25], matching the values obtained in this study by TGA-DSC (Table 2).

However, volatilization may still be rate-limiting if a strong Sb_2S_3 adsorption on carbon takes place thus artificially increasing the effective energy of Sb_2S_3 evaporation. To address this remaining uncertainty, the effects of carbon on TE atomization in GFAAS were investigated, parenthetically probing the difference between mineral inclusions (with accessible carbon) and exclusions (with elemental carbon covered with inert coating). The results are shown in the next section.

Exclusions and the apparent nature of the rate limiting step. Unlike either As_2S_3 or Sb_2S_3 in regular GFAAS graphite tubes, two absorbance peaks were observed for Sb_2S_3 atomization in WO_3 -coated tubes (Fig. 2b). However, the lower temperature peak turned out to be an artifact of interactions with the coating material as it was concentration independent and did not show up in experiments using the ZrO_2 coating.

The second, pertinent peak appears at a significantly lower temperature compared to its location without coating (Fig. 1b), indicating that the separation of the simulated exclusion from the graphite in the AAS furnace tube increases sulfide volatility and facilitates its atomization. Furthermore, the E_a values obtained with coating in GFAAS using both coating materials, WO_3 and ZrO_2 , turned out to be lower than that without coating, i.e., when carbon is accessible (Table 1). The E_a obtained in GFAAS with coated tubes matched that obtained in TGA experiments for Sb_2S_3 evaporation without carbon (Table 2). Therefore, the presence of a coating appears to protect this sulfide from a strong adsorption on carbon, with vaporization being rate limiting. As such, antimony sulfide vaporization may be greater from excluded minerals than from included minerals during coal combustion.

The significant difference observed in the GFAAS experiments between the behavior of Sb_2S_3 and As_2S_3 appears to be due to Sb_2S_3 's stronger adsorption on carbon (Table 1). Other than this effect, the evolution of both TEs from their sulfides follows similar trends, i.e., a facile formation of their elemental forms in the gas phase, with evaporation being rate limiting.

3.4. Selenium sulfide partitioning and atomization using GFAAS

Inclusions. The observed activation energy of SeS_2 atomization is the lowest among all three TE sulfides (Table 1), suggesting that the rate limiting step is also evaporation, just as for the other two. This assumption is consistent with the even lower TGA activation energy values observed for SeS_2 volatilization, 16 ± 1 kcal/mol, which is likely lower due to sulfide adsorption on GFAAS graphite tubes.

Strong SeS_2 adsorption on carbon was confirmed by two independent experiments. First, the TGA temperature profile obtained in the presence of carbon (Fig. 3b) showed a significant shift toward higher temperatures compared to the carbon-free case (Fig. 3a). Second, as SeS_2 was found to be soluble in a non-aqueous solvent, CS_2 , in a sufficient concentration to enable GFAAS measurements, select experiments were conducted in this system. The resulting E_a

value, 56 ± 4 kcal/mol, is significantly higher than that in the presence of polysulfide matrix, 32 ± 3 kcal/mol. This difference indicates weaker SeS_2 chemical interactions with the K_2S_n melt compared to carbon, i.e., polysulfide “protects” SeS_2 from the strong adsorption on carbon thus providing a more facile path to selenium atomization. A similar protective effect of silicate was observed earlier for selenium oxide atomization in GFAAS [9].

Two Se absorbance peaks were observed in the GFAAS profile, with the first peak eluting at an even lower temperature than the second peak which also eluted at a low temperature. Given the apparent weak SeS_2 interactions with K_2S_n , the occurrence of two peaks may be explained by the apparent presence of a significant fraction of the selenium sulfide on the polysulfide melt surface as opposed to within the polysulfide melt. So while most of the SeS_2 is physically entrained in the matrix, with a slightly hindered evaporation, some evaporates earlier from the surface. This hypothesis assumes that selenium atomization, unlike that of the other two TE sulfides, occurs in the melt rather than in the gas phase. Additional evidence supporting this assumption is shown in the next section.

Likely chemical mechanism of Se atomization. A detailed examination of the SeS_2 elution profile revealed its specific and pronounced feature, an extremely low signal intensity indicating an extremely low atomization efficiency of SeS_2 compared to the other TE sulfides. This observation is underscored by comparing the GFAAS signals of selenium sulfide and selenium oxide, as shown in Fig. 1c.

The observed extremely low atomization efficiency of SeS_2 can be explained using literature data, assuming the chemical similarity of selenium and sulfur [28]. Selenium sulfide tends to form cyclic species with a varied sulfur content ($\text{Se}_n\text{S}_{8-n}$ and $\text{Se}_n\text{S}_{12-n}$) at high temperatures, which are similar to well-known S_8 sulfur clusters [29]. These molecular forms cannot be detected by GFAAS and their presence leads to extremely low absorbance values. The formation of such clusters may explain the observed promoting effect of the polysulfide matrix on selenium release from the solid phase, as it may selectively retain sulfur and enrich the vapors with selenium.

Additional details of the Se atomization mechanism may be obtained from the published thermochemical data [30]:

The low enthalpy shown in eq 5 is characteristic for evaporation and matches the E_a experimental value obtained using GFAAS. According to this equation, selenium would mostly evaporate in its molecular form. Furthermore, according to eqs 4 and 5, the Se-Se bond enthalpy in the gas phase is as high as $48 \times 2 - 33 = 63 \text{ kcal} \cdot \text{mol}^{-1}$ as calculated from eqs 4-5 using the reaction stoichiometry and Hess' law. Thus, once volatilized in its molecular form, it appears to be rather stable. This information corroborates the observed low GFAAS atomic selenium signal.

No enthalpy value is reported in the literature for the evaporation of single Se atoms from the melt that retain their atomic speciation, as this does not happen as a bulk process. However, the above described experimental observations indicate that its value is similarly low and it may occur for a small fraction of selenium atoms as they are formed in the polysulfide melt. Previous literature reports that selenium disulfide partially decomposes upon melting [29], with a very low $\Delta H_{\text{melting}}$ value, $3 \pm 1 \text{ kcal} \cdot \text{mol}^{-1}$ [28] matching that obtained in this study using DSC (Table 2). Furthermore, according to the literature, the selenium disulfide melt is composed of a mixture of selenium monosulfide existing in equilibrium with a sulfur selenium solid solution [31-33].

Thus, low-energy partial SeS_2 decomposition occurring during volatilization may be the rate limiting step for SeS_2 atomization. Perhaps multiple intermolecular interactions in the melt facilitate the temporary scission of intramolecular Se-S bonds. Most of the intermediates thus formed react back, with only a small fraction of selenium near the surface escaping via evaporation. The E_a values of Se atomization obtained by TGA and GFAAS, 15 and 30 kcal/mol, respectively, are larger than $\Delta H_{\text{melting}}$. This difference corroborates the SeS_2 melting with a significant concomitant decomposition as described above combined with adsorption on carbon as further elaborated in the next section.

Exclusions: Effects of carbon and metal oxide coating. Selenium evolution in coated graphite tubes (Fig. 2c) differs from the uncoated tubes (Fig. 1c) quantitatively (i.e., E_a) but not qualitatively, indicating that the accessibility of elemental carbon is not a significant factor for Se atomization. Due to the above-described high SeS_2 propensity to adsorption, the E_a effective value was expected to increase when the Se atomization occurs on interacting surfaces such as

coating materials. This effect was indeed observed and turned out to be pronounced, for two different coatings (Table 1). Thus, if significant non-sulfide impurities occur in either inclusions or exclusions, a delay of selenium sulfide evaporation to higher temperatures is expected.

3.5. Comparison of all three TE sulfide partitioning and atomization results

Barring minor element-specific effects, trends in the evolution of all three TEs from their sulfides upon coal combustion are similar. Specifically, the accessibility of elemental carbon as a reducing agent does not appear to be significant for any of the three TE sulfides, although carbon does appear to serve as a physical adsorbent for antimony sulfide. TE sulfide volatilization appears to be rate limiting in all three cases. Thus, due to low activation energies of either the elemental TE species or their immediate precursors, TE sulfides with a low sulfur content dominate in the gas phase even at low temperatures (as long as the temperature exceeds the boiling point of the corresponding starting TE sulfide material). This uniformity and simplicity of TE sulfide evolution is in stark contrast with the diverse atomization paths and chemistry of TE oxides reported earlier [9, 10].

One small but tangible difference is the phase in which the TE atoms are generated. It appears that while elemental arsenic and antimony are readily formed in the gas phase, selenium is unique in remaining bonded to sulfur atoms even after vaporization. Thus, the atomic selenium observed is a small fraction of the total vaporized and is primarily formed in the melt prior to vaporization. The second difference is that antimony sulfide appears to have a greater propensity to adsorb on carbon than the arsenic analog. Thus, TE evolution from sulfide inclusions and exclusions is expected to be similar with the exception of antimony where hindered evaporation may result in increased retention in the solid phase, at least until near complete carbon burnout is achieved. It is unclear whether this adsorption effect leads to lower overall Sb_2S_3 vaporization due to retention in resolidified ash particles or just to a delay in vaporization.

These conclusions were drawn mostly from the GFAAS data, and so they are applicable only when the process occurs in a reducing micro-environment. The next section discusses how the operation of TGA-DSC in the oxidizing micro-environment provided an opportunity to qualitatively investigate the influence of oxygen on TE partitioning into the gas phase.

3.6. Assessment of TE volatilization from sulfide inclusions and exclusions using TGA-DSC

The TGA and DSC data obtained for SeS_2 are shown in Figs. 3 and 4 while the qualitatively similar figures for arsenic and antimony sulfides are shown in Supplementary Figs. 1-4, respectively. The experimental setup used allowed for a variation of the residual oxygen amount in the system. Namely, at high nitrogen gas flowrate the conditions were near-anaerobic (reducing) as some oxygen diffusion might still occur in this non-sealed system; yet not *strictly* anaerobic as in GFAAS. By contrast, at a lower nitrogen flowrate the conditions in the system may qualitatively be described as microaerobic, i.e., oxidizing micro-environment.

These assumptions were verified by measuring the direction of heat flow using DSC. Exothermic reactions took place only at temperatures higher than 1000 °C, thus justifying the assumption of non-zero oxygen diffusion into the system under both scenarios when facilitated by higher temperatures. However, the reaction was found to be *endothermic* at all temperatures below 1000 °C under the above-specified conditions, both near-anaerobic and microaerobic. Furthermore, the heat flow depicted in the DSC profiles was not altered/reversed under a lower nitrogen flowrate indicating that neither carbon nor TE sulfide underwent combustion, i.e., a significant stoichiometric reaction with oxygen within the most important temperature range of TE sulfide evolution.

In contrast to the reaction with oxygen, the observed interaction of TE sulfides with elemental carbon was found to be significant. Namely, the TGA experiments conducted under microaerobic conditions (oxidizing micro-environment), i.e., with a low nitrogen flowrate, suggest that TE sulfides react with carbon chemically, as multiple peaks are present in the DSC profiles. By contrast, only a single peak is observed under similar conditions without carbon (Fig. 4a). Perhaps, the multiple peaks observed in the presence of carbon result from the increase in the crystallite size distribution along with the addition of 0.42–0.84 mm carbon particles to the TE sulfide powder. A wide size distribution is known to be a reason for similar multiple endothermic peaks in melting (or partial melting)-recrystallization processes [34].

In addition to the proposed TE sulfide *reaction* with carbon, their *desorption* from the carbon surface might cause a similar increase of the heat flow. The adsorption on carbon certainly occurs, as the TGA profiles (Fig. 3) become broader in the presence of carbon indicating a greater retention of TE sulfides at higher temperatures. This observation

corroborates similar observations made by using GFAAS. However, adsorption/desorption *per se* cannot explain the lack of having similar multiple peaks, not only in an oxidizing micro-environment, but also in a reducing micro-environment (Fig. 4). Thus, oxygen appears to be involved, even though present in less than stoichiometric amounts.

It appears that TE sulfide reactions with carbon are activated by increasing amounts of oxygen. In contrast to the direct supporting evidence obtained for this assertion in an oxidizing micro-environment, no pronounced effects of carbon were observed using DSC in a reducing micro-environment, as no distinct peaks were observed. However, indirect evidence for a similar effect occurring under lower oxygen concentrations was obtained using TGA. Table 2 shows that the activation energies for the evolution of all three TE sulfides were significantly lower in the presence of carbon under such conditions. Thus, TE evolution into the gas phase appears to be promoted rather than hindered (as it would be as a result of adsorption) in the presence of carbon. No such effects were observed using GFAAS operated under strictly anaerobic conditions (in a reducing micro-environment). Thus, even trace amounts of oxygen appear to activate carbon to enable it to react chemically with TE sulfides. This is a novel and unanticipated effect and was only discovered by using the combination of GFAAS and TGA/DSC under variable gas flowrates.

However, since the reduction of TE sulfides by carbon generates the same species, i.e., elemental TEs and unstable sulfides with a lower sulfur content, the only apparent difference due to the presence of carbon under microaerobic conditions (in an oxidizing micro-environment) is a faster and more abundant generation of these species, even at lower temperatures, and transfer of these ultimate products into the gas phase.

It is of note that microaerobic conditions during the onset of coal combustion, when most of the TEs evolve from the solid phase, are more characteristic for mineral exclusions than for inclusions due to the lack of elemental carbon in the microenvironment of exclusions. This condition also occurs in the late combustion and earlier post-combustion time period for inclusions and suggests that late evolution from these minerals may be facilitated as the micro-environment surrounding these particles transitions from very high temperature, anaerobic conditions to lower temperature, microaerobic conditions.

4. Conclusions

The accessibility of elemental carbon does not appear to play a significant role in the atomization of any of the three TE (As, Sb, Se) sulfides as a reducing agent, in a reducing micro-environment (strictly anaerobic conditions) characteristic for GFAAS. This contrasts with previous results for the analog TE oxides. Conversely, adsorption on carbon increases the transition temperature for the partitioning of all three TE sulfides into the gas phase. In particular, antimony sulfide vaporization appears to be significantly inhibited when carbon is accessible and thus vaporization may be significantly lower for Sb sulfides from mineral inclusions during the initial stages of combustion than from excluded minerals. This effect is less pronounced for selenium sulfide, despite its high propensity for adsorption, due to the “protective” effect of the polysulfide matrix. This matrix is expected to be present in real coal particles since most selenium sulfides are present in sulfide-containing minerals such as pyrites.

Sulfide evaporation appears to be rate limiting for the atomization of all three TEs whereas TE sulfide decomposition appears to be facile. A difference between the arsenic/antimony and selenium evolution is that elemental As and Sb appear to readily form in the gas phase rather than in the melt. As such, either As/Sb elemental forms or their immediate unstable precursors, TE sulfides with a low sulfur content are predominant in the gas phase if they evolve from sulfides, either from inclusions or exclusions, presuming no significant interaction with basic metal oxides in ash.

Even trace concentrations of oxygen, whose presence is characteristic of mineral exclusions as well as the transition environment for inclusions during later combustion time periods appear to activate elemental carbon enabling the chemical reduction of TE sulfides. This effect may result in faster generation of gas phase TEs during coal combustion but has minimal effect on the short-term gas phase speciation resulting from TE sulfide partitioning.

5. Acknowledgements

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a)

b)

c)

Figure 1. The absorbance signal for TE oxide or chloride, 200 ppb, and TE sulfide 200 ppb in K_2S_n obtained in uncoated graphite tubes. (a) Arsenic(III) oxide and sulfide, (b) antimony(III) chloride and sulfide and (c) selenium(IV) oxide and sulfide.

a)

b)

c)

Figure 2. The absorbance signal for TE oxide or chloride, 200 ppb, and TE sulfide, 200 ppb in K_2S_n obtained in tungsten (VI) oxide coated graphite tubes. (a) Arsenic(III) oxide and sulfide, (b) antimony(III) chloride and sulfide and (c) selenium(IV) oxide and sulfide.

Figure 3. The TGA temperature profiles for (a) SeS_2 and (b) SeS_2 with activated carbon in oxidizing and reducing micro-environments.

Figure 4. The DSC profiles for (a) SeS_2 and (b) SeS_2 with activated carbon in oxidizing and reducing micro-environments.

Table 1. Activation Energies for Trace Element Sulfides in the presence of 0.11 mg/mL Potassium Polysulfide Matrix in Uncoated, Tungsten (VI) and Zirconia (IV) Oxide Coated Graphite Tubes.

Compound	Conc., ppb ^a	E _a , kcal/mol		
		Uncoated	WO ₃ -coated	ZrO ₂ -coated
As ₂ S ₃ with K ₂ S _n	100	35±3	46±3	68±2
	150	34±1	50±7	58±3
	200	38±1	54±2	58±3
	300	40±4	50±5	57±3
	400	37±3	43±4	53±2
Sb ₂ S ₃ with K ₂ S _n	100	44±4	63 39	25±1
			46 39	
			40 41	
	150	57±3	47 41	27±1
			51 28	
			60 27	
	200	55±5	46 38	28±2
			36 33	
			58 22	
	300	49±4	34 34	26±2
			72 25	
			51 35	
SeS ₂ with K ₂ S _n	100	b	54 33	24±1
			48 29	
			52 24	
			80±4	
			61±10	
SeS ₂ with K ₂ S _n	150	28±1	61±3	63±3
	200	31±4	48±5	64±2
	300	32±4	51±5	60±1
	400	36±2		60±1

^a Recalculated for the injection volume of 20 µL

^b Could not be determined because the absorbance value was too small

Table 2. Activation energies and reaction enthalpies determined for TE sulfides using TGA-DSC in reducing and oxidizing micro-environments,^a respectively, with and without elemental carbon (C).

Form	Transition temperature, °C		Activation energy ^b , kcal·mol ⁻¹		Reaction enthalpy ^b , kcal·mol ⁻¹	
	Without C	With C	Without C	With C	Without C	With C
As ₂ S ₃	495	593	31 ^c	15	29	ND ^f
Sb ₂ S ₃	830	825	32 ^d	18	34	ND ^f
SeS ₂	387	575	16	13	3 ^e	ND ^f

^a TGA data could not be quantified in an oxidizing micro-environment due to the occurrence of multiple overlapping processes; DSC data could not be quantified in a reducing micro-environment due to a lack of integrable peaks

^b The experiments were performed in duplicate

^c Reported value [25, 27]: 20-22 kcal·mol⁻¹

^d Reported value [16, 25]: 32 kcal·mol⁻¹

^e Reported value of melting enthalpy [28]: 3 kcal·mol⁻¹

^f Could not be determined by the DSC unit due to the occurrence of multiple overlapping peaks

6. Figure Captions

Figure 1. The absorbance signal for TE oxide or chloride, 200 ppb, and TE sulfide 200 ppb in K_2S_n obtained in uncoated graphite tubes. (a) Arsenic(III) oxide and sulfide, (b) antimony(III) chloride and sulfide and (c) selenium(IV) oxide and sulfide.

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Supplementary Figure 1. The TGA temperature profiles for (a) As_2S_3 and (b) As_2S_3 with activated carbon in oxidizing and reducing micro-environments.

Supplementary Figure 2. The TGA temperature profiles for (a) Sb_2S_3 and (b) Sb_2S_3 with activated carbon in oxidizing and reducing micro-environments.

Supplementary Figure 3. The DSC profiles for (a) As_2S_3 and (b) As_2S_3 with activated carbon in oxidizing and reducing micro-environments.

Supplementary Figure 4. The DSC profiles for (a) Sb_2S_3 and (b) Sb_2S_3 with activated carbon in oxidizing and reducing micro-environments.

7. References

- [1] Tang Q, Liu G, Yan Z, Sun R. Distribution and fate of environmentally sensitive elements (arsenic, mercury, stibium and selenium) in coal-fired power plants at huainan, anhui, china. *Fuel* 2012; 95: 334-9.
- [2] Tomeczek J, Palugniok H. Kinetics of mineral matter transformation during coal combustion. *Fuel* 2002; 81: 1251-8.
- [3] Raask E. The mode of occurrence and concentration of trace elements in coal. *Prog Energy Combust Sci* 1985; 11: 97-118.
- [4] Jassim E, Benson SA, Bowman FM, Seames WS. The influence of fragmentation on the behavior of pyrite particles during pulverized coal combustion. *Fuel Proc Technol* 2011; 92: 970-6.
- [5] Liu Y, Gupta R, Wall T. Ash formation from excluded minerals including consideration of mineral–mineral associations†. *Energy Fuels* 2007; 21: 461-7.
- [6] Yan L, Gupta RP, Wall TF. A mathematical model of ash formation during pulverized coal combustion. *Fuel* 2002; 81: 337-44.
- [7] Bailey CW, Bryant GW, Matthews EM, Wall TF. Investigation of the high-temperature behavior of excluded siderite grains during pulverized fuel combustion. *Energy Fuels* 1998; 12: 464-9.
- [8] Raeva AA, Pierce DT, Seames WS, Kozliak EI. A method for measuring the kinetics of organically associated inorganic contaminant vaporization during coal combustion. *Fuel Proc Technol* 2011; 92: 1333-9.
- [9] Raeva AA, Klykov OV, Kozliak EI, Pierce DT, Seames WS. In situevaluation of inorganic matrix effects on the partitioning of three trace elements (as, sb, se) at the outset of coal combustion. *Energy Fuels* 2011; 25: 4290-8.
- [10] Raeva AA, Dongari N, Artemyeva AA, Kozliak EI, Pierce DT, Seames WS. Experimental simulation of trace element evolution from the excluded mineral fraction during coal combustion using gfaas and TGA-DSC. *Fuel* 2014; 124: 28-40.
- [11] Kos CHP, R.P.E.; Bos, P.; Kuene, J.G. , Geochemistry of sulfides in coal and microbial leaching experiments, in: *Kohlenwissenschaft; internationale Tagung, Gluckauf, Dusseldorf*, 1981.

- [12] Granite EP, Henry. Photochemical removal of mercury from flue gas. *Ind Eng Chem Res* 2002; 41: 5470-6.
- [13] Granite EP, Henry; Hargis, Richard. Novel sorbents for mercury removal from flue gas. *Ind Eng Chem Res* 2000; 39: 1020-9.
- [14] Presto AA, Granite EJ. Impact of sulfur oxides on mercury capture by activated carbon. *Environ Sci Technol* 2007; 41: 6579-84.
- [15] Presto AA, Granite EJ, Karash A. Further investigation of the impact of sulfur oxides on mercury capture by activated carbon. *Ind Eng Chem Res* 2007; 46: 8273-6.
- [16] Padilla R, Ramírez G, Ruiz MC. High-temperature volatilization mechanism of stibnite in nitrogen-oxygen atmospheres. *Metall Mater Trans B* 2010; 41: 1284-92.
- [17] Laborda F, Medrano J, Cortés JI, Mir JM, Castillo JR. Comparison of palladium and zirconium treated graphite tubes for in-atomizer trapping of hydrogen selenide in hydride generation electrothermal atomization atomic absorption spectrometry. *Spectrochim Acta, Part B* 1999; 54: 343-53.
- [18] Garboś S, Wałcerz M, Bulska E, Hulanicki A. Simultaneous determination of Se and As by hydride generation atomic absorption spectrometry with analyte concentration in a graphite furnace coated with zirconium. *Spectrochim Acta, Part B* 1995; 50: 1669-77.
- [19] Fritzsche H, Wegscheider W, Knapp G, Ortner HM. A sensitive atomic-absorption spectrometric method for the determination of tin with atomization from impregnated graphite surfaces. *Talanta* 1979; 26: 219-26.
- [20] Friedman R, Principles of fire protection chemistry and physics, Third Edition ed., Jones and Bartlett Publishers, 2008.
- [21] Smets B. Atom formation and dissipation in electrothermal atomization. *Spectrochim Acta, Part B* 1980; 35: 33-42.
- [22] Hillier J, Bezzant T, Fletcher TH. Improved method for the determination of kinetic parameters from non-isothermal thermogravimetric analysis (TGA) data. *Energy Fuels* 2010; 24: 2841-7.
- [23] Vickrey TM, Buren MS. Factors affecting selenium atomization efficiency in graphite furnace atomic absorption. *Anal Lett* 1980; 13: 1465-85.
- [24] Vickrey TM, Harrison GV, Ramelow GR. Treated graphite surfaces for determination of tin by graphite furnace atomic absorption spectrometry. *Anal Chem* 1981; 53: 1573-6.

- [25] Dauletbakov TS, The kinetics of arsenic and stibium sulfides' exhalation in the boiled layer, in: UDK 6227, Kazah National Technical University after K.I. Satpayev, 2008.
- [26] Kerr JA, Crc handbook of chemistry and physics, 81st ed., CRC Press, Boca Raton, Florida, USA, 2000.
- [27] Town JWRPD, Thermogravimetric and distillation studies on mercury, antimony and arsenic sulfides, in, Mineral University Research Laboratory, University of Alaska, 1975.
- [28] Laitinen R, Niinistö L. Thermal behaviour of the monoclinic allotropes γ -sulfur and α -selenium and some structurally related sulfur-selenium compounds. *J Therm Anal* 1978; 13: 99-104.
- [29] Steudel R, Laitinen R, Cyclic selenium sulfides, in: *Inorganic ring systems*, Springer Berlin Heidelberg, 1982, pp. 177-97.
- [30] Rossini FD, Selected values of chemical thermodynamic properties, U.S. Govt. Print. Off., Washington, 1952.
- [31] Geoffroy N, Demopoulos GP. The elimination of selenium(IV) from aqueous solution by precipitation with sodium sulfide. *J Hazard Mater* 2011; 185: 148-54.
- [32] Bioassay of selenium sulfide for possible carcinogenicity (dermal study), in: *Carcinogenesis Testing Program*, 1980, pp. 1-83.
- [33] Mitchell SC, Nickson RM, Waring RH. The biological activity of selenium sulfide. *Sulfur reports* 1993; 13: 279-89.
- [34] Alamo R, Mandelkern L. Origins of endothermic peaks in differential scanning calorimetry. *J Polym Sci, Part B: Polym Phys* 1986; 24: 2084-105.

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			60 27	
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			36 33	
			58 22	
	300	49±4	34 34	26±2
			72 25	
			51 35	
	400	52±5	54 33	24±1
			48 29	
			52 24	
SeS ₂ with K ₂ S _n	100	^b	80±4	60±1
	150	28±1	61±10	63±3
	200	31±4	61±3	64±2
	300	32±4	48±5	60±1
	400	36±2	51±5	60±1

^a Recalculated for the injection volume of 20 µL

^b Could not be determined because the absorbance value was too small

Table 2

Table 2. Activation energies and reaction enthalpies determined for TE sulfides using TGA-DSC in reducing and oxidizing micro-environments,^a respectively, with and without elemental carbon (C).

Form	Transition temperature, °C		Activation energy ^b , kcal·mol ⁻¹		Reaction enthalpy ^b , kcal·mol ⁻¹	
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^a TGA data could not be quantified in an oxidizing micro-environment due to the occurrence of multiple overlapping processes; DSC data could not be quantified in a reducing micro-environment due to a lack of integrable peaks

^b The experiments were performed in duplicate

^c Reported value [21, 23]: 20-22 kcal·mol⁻¹

^d Reported value [12, 21]: 32 kcal·mol⁻¹

^e Reported value of melting enthalpy [24]: 3 kcal·mol⁻¹

^f Could not be determined by the DSC unit due to the occurrence of multiple overlapping peaks

Figure 1a

Figure 1b

Figure 1c

Figure 2a

Figure 2b

Figure 2c

Figure 3a

Figure 3b

Figure 4a

Figure 4b