



Evaluation of sampling methods for sulfur speciation in volcanic gases



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ABSTRACT

Determination of H₂S and SO₂ in fumarolic gases is necessary to predict volcanic activities. This study evaluated three gas sampling methods (CdS precipitation, Ag₂S precipitation, and I₂ oxidation) using artificial fumarolic gases with known compositions. H₂S was initially fixed as CdS(s) or Ag₂S(s) in the sulfide precipitations and S(0) in the I₂ oxidation. On the other hand, SO₂ was collected as dissolved species (SO₃²⁻ and SO₄²⁻). The Ag₂S precipitation, which did not allow HCl determination in fumarolic gases by forming AgCl(s), significantly underestimated H₂S and SO₂ due to the entrained loss of analytes as a result of water vaporization during H₂O₂ treatment. The I₂ oxidation, which required duplicate sampling for complete analysis of H₂S and SO₂, tended to overestimate SO₂ probably due to difficulties in separating S(0) particles from solutions. The CdS precipitation produced more satisfactory H₂S and SO₂ recoveries than the other methods. Additionally, the effect of delayed sample treatment was assessed by comparing H₂S-to-SO₂ molar ratios resulting from immediate and one-week-delayed treatments after gas collection. The delayed treatment significantly lowered the ratios in the CdS precipitation likely due to the susceptibility of CdS(s) to oxidation. In the meanwhile, such an effect was minimal in I₂ oxidation. Similar results were also observed in the field evaluation of fumarolic gases at Mt. Hakone. Along with detailed sampling and treatment procedures, the causes for unsatisfactory H₂S and SO₂ recoveries were discussed in the context of the underlying reaction schemes as well as potential experimental artifacts. Thus, this study helps to select and further modify appropriate gas sampling methods to meet specific needs.

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1. Introduction

Fumarolic gas compositions are generally considered to be indicative of volcanic activities (Bruno et al., 2001; Ohba et al., 2010; López et al., 2013; Werner et al., 2013). The compositions of fumarolic gases provide useful information on the origin and source of magmas (Giggenbach, 1996; Capasso et al., 1997; Giammanco et al., 1998). Previously, abrupt changes in the composition of fumarolic gases have been reported at the imminence of volcanic eruption (Oskarsson, 1984; Fischer et al., 1996; Aiuppa and Federico, 2004; Capasso et al., 2005). The emission rates of fumarolic gases are much higher in the eruptive period of volcanoes than in the quiescent period. Besides higher emission rates of individual gases, the ratios among them are time-varying since the solubility of fumarolic gases in magma melts is different from one another (Menyailov, 1975; Bruno et al., 2001; Burton et al., 2007; Aiuppa et al., 2009). In addition, soil gases and hot spring waters have been monitored to have supplementary information on the magmatic activity because the compositions of both fluids are affected by rising volcanic gases (Inguaggiato

et al., 2000, 2005, 2011a,b, 2012a; Carapezza et al., 2009; Giammanco et al., 2013).

In general, H₂O, CO₂, sulfur, HCl, and HF are the major components in fumarolic gases, among which sulfur is mainly present as H₂S and SO₂ (Montegrossi et al., 2001; Lee et al., 2005). Due to the great sensitivity of H₂S and SO₂ to temperature, redox conditions, and hydrothermal interactions, the determination of their speciation is of critical importance in evaluating both volcanic activities and fluid interactions (Ossaka et al., 1980; Montegrossi et al., 2001). The relative concentrations of both sulfur species are largely determined by temperature, pressure, and redox conditions (Giggenbach, 1987). While SO₂ becomes dominant with increasing temperature and decreasing pressure under oxidizing conditions (Giggenbach, 1996), H₂S is prevalent at low-temperature fumaroles or solfataras arising from deep hydrothermal systems (Giggenbach, 1980). In this regard, low SO₂-to-H₂S ratios indicate the re-equilibrium of magmatic gases with reducing hydrothermal fluids at low temperatures (Giggenbach, 1987; Symonds et al., 1996). Thus, not only the sum of SO₂ and H₂S but each sulfur species needs to be determined for better prediction of volcanic activities (Ossaka et al., 1980; Ohba et al., 1994; Montegrossi et al., 2001; Werner et al., 2013). Right before the eruption of Mt. Kusatsu-Shirane in 1976, a sudden increase in the SO₂-to-H₂S ratio was observed in fumarolic gases

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(Ossaka et al., 1980). Besides this ratio, other ratios between each sulfur species and other gases can be used as potential indicators for volcanic eruption. Aiuppa et al. (2009) reported an increased CO₂-to-SO₂ ratio before the 2007 eruption of Mt. Stromboli. Also, the ratios of SO₂-to-HCl and SO₂-to-HF were found to increase right before paroxysmal events at Mt. Stromboli (Aiuppa, 2009). Concentrations of SO₂ and H₂S have also been used to determine the apparent equilibrium temperature (AET) based on the following reaction (Ohba et al., 1994):



AET is higher than the temperature measured at the outlet of a fumarole, which tends to be strongly affected by interactions with hydrothermal systems. Accordingly, using AET as well as the fumarole outlet temperature, one can better assess volcanic activities. Many volcanoes contain the hydrothermal water that dissolves fumarolic gases (Capasso et al., 2001; Takano et al., 2008; Federico et al., 2010). The scrubbing by hydrothermal water lowers SO₂ concentrations to greater extents than H₂S concentrations. When the influence of hydrothermal systems is strong, an increase in the total sulfur emission from fumaroles may not be noticed despite the increased volcanic activities. In such a case, it is useful to selectively monitor H₂S due to its less scrubbing tendency than SO₂.

To date, great efforts have been made to develop accurate and reliable techniques for determining volcanic gas compositions. According to the recent IAVCEI field workshops (Giggenbach and Matsuo, 1991; Shinohara, 1999; Giggenbach et al., 2001), however, significant variations in volcanic gas compositions from the common fumaroles were encountered among different groups and different methods. In those studies, such variations were mainly attributed to sampling artifacts: the reaction of acid gases with sampling equipment and gas condensation within sampling trains. Considering the potential of redox reactions among sulfur species and those with other gases (e.g., O₂), other factors including the type of sampling media (absorption solutions) and sample treatments need to be considered as possible accounts for the variations in sulfur speciation.

To determine sulfur speciation, the direct gas sampling using alkaline absorption solutions (e.g., concentrated NaOH, KOH, and NH₄OH) has been frequently used (Giggenbach, 1975; Sortino et al., 2006; Mioduszewski and Kress, 2008). In this approach, acidic gases (CO₂, SO₂, H₂S, HCl, and HF) dissolve into the solutions while non-condensable gases (He, Ar, N₂, H₂, and CH₄) do not dissolve. Depending on the type of absorption solutions, several methods are available for determination of sulfur speciation in fumarolic gases. A common method involves the use of evacuated Giggenbach bottles partially filled with NaOH (or KOH) solutions and the subsequent analysis of sulfur species by iodometric titration (Giggenbach and Goguel, 1989). By this method, both SO₂ and H₂S dissolve into the alkaline solutions:



This method, despite its frequent usages, cannot prevent the dissolved SO₂ and H₂S from undergoing redox reactions (Giggenbach et al., 2001). For example, the dissolved H₂S will be oxidized when O₂ is included in volcanic gases or absorption solutions are exposed to the air prior to sample analysis (Giggenbach et al., 2001). Also, hypoiodite (IO⁻), produced via disproportionation of I₂ in strongly alkaline solutions during iodometric titration, can oxidize all possible sulfur species into SO₄²⁻, thus making other sulfur species including elemental sulfur miscounted as SO₂ and H₂S (Giggenbach, 1975). If H₂S is fixed as a stable intermediate that is readily separable from the dissolved SO₂, such oxidation can be avoided. In this study, three methods involving different H₂S intermediates were considered to determine sulfur speciation. The first method was the cadmium sulfide (CdS) precipitation, which

utilized NaOH solutions containing Cd(CH₃COO)₂, Cd(ClO₄)₂, or Cd(OH)₂ (Piccardi, 1982; Montegrossi et al., 2001; López et al., 2013; Lee et al., 2013). In this method, H₂S reacted selectively with Cd²⁺ to precipitate as CdS(s):



The second method was the silver sulfide (Ag₂S) precipitation, which utilized NH₄OH solutions containing AgNO₃ (Giggenbach and Goguel, 1989; Aiuppa et al., 2005; Inguaggiato et al., 2012b). In the Ag₂S precipitation, SO₂ dissolved into alkaline solutions via Reaction (2), whereas H₂S reacted with Ag⁺ to form Ag₂S(s):



Since metallic trace elements were not analyzed, NaOH solutions were used instead of NH₄OH solutions to have alkaline pH conditions (Sortino et al., 2006). The third method was the iodine (I₂) oxidation by which fumarolic gases were independently sampled into both NaOH and KI–KIO₃ solutions (Ozawa, 1968; Ohba et al., 1994; Lee et al., 2005, 2008). Fumarolic gases were collected into alkaline solutions to determine the sum of SO₂ and H₂S, and they were also allowed to pass through KI–KIO₃ acid solutions to quantify their ratio. In the acidic solutions, SO₂ and H₂S were oxidized by I₂ to produce SO₄²⁻ and elemental sulfur S(0), respectively:



Note that elemental sulfur did not undergo further oxidation by I₂. In iodine solutions, SO₄²⁻ could be separated from S(0) by filtration or centrifuging. Besides its production via H₂S oxidation by I₂, S(0) might be included in fumarolic gases as a result of secondary interactions between SO₂ and H₂S (Yang et al., 2003; Lee et al., 2005):



In acidic iodine solutions, thus, S(0) produced via Reaction (7) could not be distinguished from that produced via Reaction (8). As discussed later, alkaline absorption solutions could be used to determine the amount of S(0) produced via Reaction (8). Given that S(0) is a predominant sulfur species at low temperature (Giggenbach and Matsuo, 1991), Reaction (8) becomes more favorable within sampling trains where the temperature drops below 100 °C, thus altering the sulfur speciation (Giggenbach et al., 2001). Such an artifact should be encountered regardless of sampling methods.

When collecting fumarolic gases using alkaline absorption solutions, one can use either evacuated bottles or bubbling traps (Giggenbach and Matsuo, 1991; Giggenbach et al., 2001). Of the two, evacuated bottles were chosen here since it was difficult to keep the atmospheric O₂ from dissolving into alkaline solutions using bubbling traps. On the other hand, when collecting fumarolic gases into iodine solutions, bubbling traps are preferred (Ozawa, 1968; Ohba et al., 1994; Lee et al., 2005, 2008) given that S(0), the H₂S intermediate in the I₂ oxidation method, is quite stable even under oxic conditions. Although not further discussed, H₂S can be selectively fixed as As₂S₃(s) in As₂O₃ solutions (Giggenbach, 1975) and ZnS(s) in zinc acetate solutions (Giggenbach and Goguel, 1989). Also, the use of zinc acetate and barium chloride solutions in series allows to fix both H₂S and SO₂ as ZnS(s) and BaSO₄(s), respectively (Menyailov et al., 1986; de Moor et al., 2013).

Although several methods are available for determination of sulfur species in fumarolic gases, few studies have evaluated and compared their accuracy and reliability. This may be in part due to lacks in reference standards of sulfur species. Moreover, few studies have provided the detailed procedures for the collection and analysis of fumarolic

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