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In situ speciation of sulfur vapors by X-ray absorption near edge structure spectroscopy

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ABSTRACT

Despite the tremendous importance for geologic systems, there is limited knowledge of sulfur-containing gas-phase geochemical reactions that take place at elevated temperatures, including up to 1000 K. This deficit is at least partly caused by a lack of suitable experimental techniques to monitor and quantify potential reactions. We developed a new furnace design that can heat solid samples to specific temperatures while in situ X-ray absorption spectra of the gas-phase species are collected at the sulfur K-edge at about 2400 eV for X-ray absorption near edge structure (XANES) spectroscopy. Our experimental design improves previous furnace systems developed to generate sulfur vapors for spectrometry measurements and earlier sulfur XANES spectroscopic analyses of sulfur-containing gases and vapors. The new design minimizes contamination by air, water vapor, and stainless steel. Our results demonstrate that vapors emitted from elemental sulfur heated to different temperatures are similar to previous findings, but we can now resolve long-held interpretative discrepancies for sulfur vapor speciation, some of which resulted from the misidentification of vapors due to reactions between the sulfur vapors and furnace materials. We also used the new design to quantify the sulfur vapor species produced from elemental sulfur reacted with water over a range of temperatures. At low temperatures, like 363 K (~90 °C), the gas consisted of different sulfur species, whereas at temperatures greater than 550 K (~280 °C), the gas present in the furnace was only SO_2. These quantitative findings show promise that future reaction kinetics can be done by using our experimental spectrometry system.

1. Introduction

Sulfur gases and vapors are highly reactive species in metamorphic reactions and the biogeochemical sulfur cycle (e.g., Steudel et al., 2003; Tomkins, 2010). Hydrogen sulfide (H_2S) dynamics have been intensely studied, due in part to their importance in hydrocarbon dilution, metal sulfide precipitation, toxicity, and corrosion processes (Mougina et al., 2007), but other sulfur gases have gone virtually unrecognized (Wong et al., 2002; Steudel et al., 2003). Our limited understanding of sulfur gases and vapors in geologic systems is at least partly due to a paucity of suitable techniques to monitor and identify gas-phase sulfur species (Vairavamurthy et al., 1995). Primarily identified from modeling, mass spectrometer molecular ionization experiments, and other spectral studies (e.g., Meyer et al., 1972; Rau et al., 1973; Meyer, 1976; Steudel et al., 2003), sulfur vapors can be generated in varying quantities and compositions from sulfur-bearing solids, like elemental sulfur and pyrite, during heating (Kirilov et al., 1994; Wong et al., 2002; Steudel, 2003; Steudel et al., 2003). As was reported by Rau et al. (1973), sulfur vapor species produced from solid elemental sulfur can include S_2 to S_8, with S_8 accounting for >90% of the gas at low temperature, and S_6 and S_7 comprising the remainder; as temperature increases, the contribution of S_8 decreases and S_2 becomes the most abundant species above 1000 K. In contrast, heating pyrite to temperatures >300 °C results in up to seven vapor S species and non-stoichiometric iron sulfides, with S_2 being considered the predominant species (Kirilov et al., 1994). H_2S and SO_2 gases can also be generated at relatively low temperatures if precursor solid phases interact with organic matter or water. Understanding what roles sulfur gases and vapors play in sedimentary systems, and being able to quantify reactions and interactions among gases and minerals, water, or other gas phases, requires methods that can not only experimentally generate a range of sulfur gases and vapors but also measure byproducts of the reactions.

To our knowledge, there have been just a few examples where vapor spectra of sulfur-containing compounds have been recorded at the

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S K-edge using X-ray absorption near edge structure (XANES) spectroscopy (Hormes et al., 1986; Prange et al., 2002a, b). XANES is one of the most efficient tools to study sulfur speciation in biogeochemical systems. In earlier investigations, compounds analyzed by XANES existed as gases at room temperature (e.g., SF_6 and H_2S) or as liquids with high vapor pressures (Hormes et al., 1987). The first known experiments to produce gas-phase spectra from heated elemental sulfur were attempted by two groups. Durand et al. (1996) used a furnace and measured the pure phases S_2 in the gas phase, and of α-sulfur (S_8) and ω-sulfur in the solid phase. Rühl et al. (2002) measured total cation yields from a sulfur vapor "beam" that produced results inconsistent with the earlier study, which we consider to be a consequence of the experimental design.

To attempt to resolve these contradicting results, and to simulate diagenetic, and possibly catagenic, geochemical reactions between sulfur vapors and water, we designed an experimental system that utilizes a modified furnace simultaneously interfaced with a XANES beam line to spectroscopically measure and speciate vapors generated from incrementally heated solid elemental sulfur. Clearly, measuring spectra of sulfur gases and vapors at low X-ray energies of the sulfur K-edge (~2400 eV) and simultaneously applying high temperatures require specialized instrumentation, including a beam line without a Be window where the furnace can operate at atmospheric pressure of He while being separated by a thin window from the monochromator that runs under ultra-high vacuum conditions on the same beam line. There are serious technical problems and a wide range of potential ways that experiments can become contaminated, such as from air, water vapor, and interactions with the furnace material.

The approach that we developed is different from previous furnaces used for XANES spectroscopic analyses because we optimized the instrumentation to reduce potential contamination. Here, we demonstrate that compositionally distinguishable vapors emitted from elemental sulfur heated to different temperatures are similar to previous findings (Durand et al., 1996; Rühl et al., 2002). The results provide new insight for resolving geochemical discrepancies in the interpretation of sulfur vapor speciation, as well as provide a foundation from which a number of questions regarding the physics of sulfur gases can be addressed. In separately conducted experiments, vapors produced from elemental sulfur reacting with water over a range of temperatures reveal that the new experimental design can solve kinetic problems in geologic systems that involve sulfur gases and vapors, or be used for industrial applications like in mining (Frasch process) and desulfurization of natural gas (Claus process) (e.g., Steudel et al., 2003).

2. Materials and methods

2.1. The furnace system

The design of our furnace system had to meet the following requirements:

- Be chemically resistant to vapors and inert to sometimes reactive gas-phase components,
- Tolerate a temperature range of 293 to >1000 K (20 to >700 °C),
- Maintain stable conditions for taking spectra for at least 3 to 4 h, and
- Allow measurements at low X-ray energies, specifically the sulfur K-edge.

Few furnace systems are described in the literature that fulfill at least some of these requirements. Bouisset et al. (1991), for example, describe a high temperature King furnace that was used for recording the gas-phase spectra of Si in SiO vapor. Aside from being of complicated construction, the materials that come into contact with the vapor (e.g., tantalum) are most likely not resistant to sulfur vapors at higher pressures and temperature, even though this furnace was also used by Durand et al. (1996) for their sulfur gas-phase experiments. Over the years, simplistic (Prešeren et al., 1996) and complicated (Mihelič et al., 2002) furnace designs to take X-ray absorption spectra of monometallic vapors were described, one being a double cell furnace for measuring Zn vapor (Mihelič et al., 2002) and another being based on principles (e.g., the "heat pipe principle") (Prešeren et al., 1996, 1999) that are also unsuitable for sulfur compounds.

Fig. 1 shows the furnace setup as we used it for the experiments described herein. The central part of the furnace was a ~50 cm long stainless steel tube of 40 mm inner diameter, with standard KF 40 vacuum flanges welded on both ends. For each experiment, we used a quartz tube (~50 cm long, with 3 mm wall thickness) inserted into the steel furnace to prevent the interaction of vapors with the stainless steel furnace surfaces. The outside of the central part of the furnace tube was tightly coiled with ~1 m of a heating wire (THERMOCOAX®, Alpharetta, Georgia, USA) (Fig. 1a) to allow for currents up to 10 A and temperatures up to ~1300 K (~1000 °C). The furnace temperature was measured by a thermocouple attached to the surface at the coil center using a hose clip. For measuring and controlling the temperature, the output signal of the thermocouple was fed into a SOLO SL4848 temperature controller that was connected to an AMETEK Sorensen XHR100-10DC power supply. During operation, the furnace and heating wire assembly was wrapped with aluminum foil as a heat shield (Fig. 1b). This setup allowed the temperature to be set and held constant to ±0.5 °C during XANES spectra collection at a specified temperature.

During the early design phase of our work, we measured the temperature inside of the quartz tube at the sample position using a second thermocouple to compare the temperature at the actual sample position (inside) with the temperature measured by the coil thermocouple (external). Using the arrangement of coiled heating wire shown in Fig. 1, including thermo-shielding with aluminum foil, temperatures at

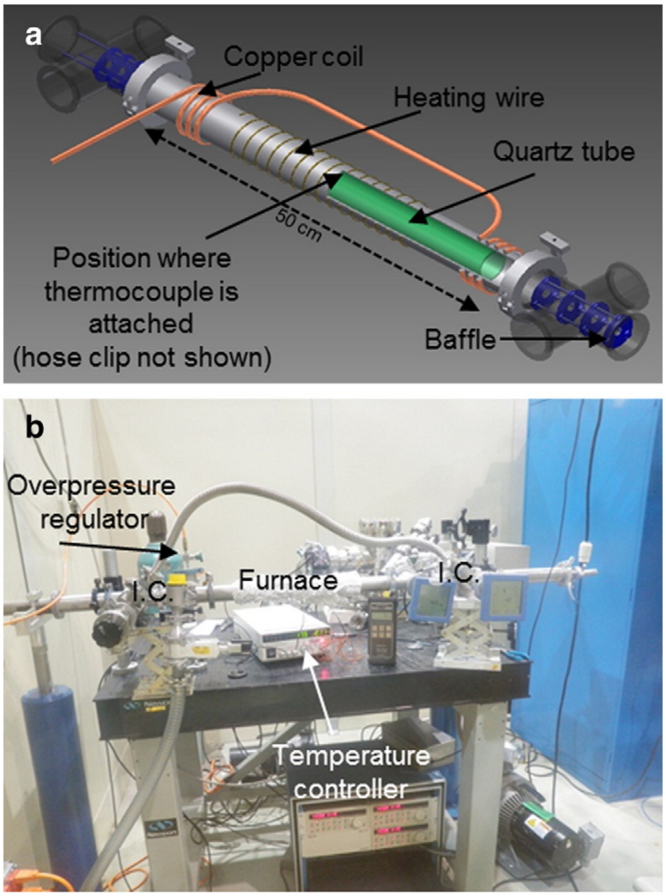

Fig. 1. a) Experimental design of furnace, heating and cooling coils, quartz tube, baffles, and cross-pieces. This equipment was installed between the ionization chambers. b) Analytical setup with furnace installed on DCM beamline between ionization chambers (I.C.).