Sulfur K-edge XANES study of S sorbed onto volcanic ashes

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Abstract. Powders of four synthetic glasses of volcanic composition, a silica glass and crystalline quartz were equilibrated with SO2 to study the speciation of S sorbed onto their surface. These samples mimic the aerosols injected into the atmosphere during volcanic eruptions. Volcanic sulfur is known to globally affect the Earth’s climate with an opposite effect to CO2. However, absorption on ashes may reduce the amount of sulfur entering the stratosphere. S K-edge micro-XANES (μXANES) spectra and μXRF maps were collected at the LUCIA beamline (SOLEIL) at the SLS (Switzerland). When photoreduction is minimized, SO2 is sorbed mostly as sulfates moieties. The sorption of S is controlled by the surface structure of the powders probed. Presence of defects, non-bridging oxygens and network-modifiers (alkali and alkali-earths) enhance S-sorption as sulfate moieties onto the powders surface. Therefore, the quantity of S released to the atmosphere is highly dependant on the type of ash produced during eruptions that help to better model the climatic impact of volcanic S.

1. Introduction
Volcanic sulfur is known to globally affect the Earth’s climate [1], with an opposite effect to CO2. Large amounts of sulfur may be emitted during volcanic eruptions, predominantly as SO2, and particularly in large explosive eruptions (e.g., Tambora in 1813, Krakatau in 1883, Mt. St. Helens in 1980). However, SO2 is a highly reactive gas and depending on the interactions of SO2 with ashes during eruptions, the gas may be removed from the eruption column before it reaches the stratosphere. Therefore, it is important to quantify the adsorption and speciation of S on volcanic ashes. Volcanic ashes are composed of micrometric to millimetric grains of volcanic rocks (composed mostly by micron-sized silicate crystals disseminated into an amorphous glass), projected violently into the atmosphere during explosive eruptions. Because of the relatively low amounts of S present onto the surface of the grains of volcanic ash, only spectroscopic methods can be used to ascertain the speciation of S. Hence, infra-red and XAFS spectroscopies are appropriate tools to identify the speciation of S on those samples. XAFS spectroscopy has the advantage to be directly sensitive to oxidation state, as its probes the electronic structure of S [2-11], which is dependant on its speciation

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Therefore, we studied a μ-XRF/μ-XANES study at the sulfur K-edge of samples exposed to a SO$_2$ atmosphere which special emphasis on model compounds and photoreduction artifacts.

1. Experimental

Five samples were prepared, crystalline quartz and four glasses that mimic magmas injected into the atmosphere during explosive events (arc-volcanism). The four glasses compositions include andesite, dacite, rhyolite and silica. The glasses were synthesized from oxide and carbonate mixtures. The mixtures were first decarbonated by slow heating to 1100°C. The charge was then molten in a Pt crucible at 1600°C and quenched in water to produce a crystal-free glass. The glasses were then ground in a planetary mill to grain sizes of a few micrometers or less. The surfaces were then saturated with SO$_2$ by immersing in SO$_2$ gas at 20°C and 1 bar for 24 hours. 35 model compounds of S were run in parallel to better compare the experiments for the glasses.

Sulfur K-edge micro-XANES (μXANES) spectra and μXRF maps were collected in 2007 at the LUCIA beamline [12] (SOLEIL) at the SLS (Switzerland). The storage ring is operating at 2.4 GeV with 400 mA injected electronic currents. Double-crystals Si(111) monochromator (energetic resolution ~ 0.3 eV at 3 keV) were used and K-B mirrors focused the X-ray beam to 3x3 μm$^2$. Harmonics were rejected using Ti-coated mirrors. Flux on the sample is 2 x 10$^{12}$ ph/s at 400 mA injected currents and 2 keV. Pellets of powders were set into a primary vacuum. A SDD detector collected the μ-XANES spectra using the S-K$_\alpha$ fluorescence signal. Total electron yield (TEY) quick-μ-XANES spectra (24 sec/spectra) were also collected to monitor photoreduction of S induced by the X-ray beam. Energetic resolution is estimated to be 0.5 eV while lateral resolution was about 5 μm.

In addition, 35 models compounds of sulfur were studied, ranging from reduced sulfides (S(-II), S(-I)) to sulfates (S(VI)). Special emphasis was given to the features near 2478 eV (labeled * in Figs 1-2), related to S(IV) [2-10] and S(VI) [11]. If most authors report that the S K-edge is sensitive to the “redox of S”, the XANES is more indicative of the actual charge transfer around S (see [2]), which is only roughly related to the actual “redox of S” (whatever this macroscopic chemical concept physically means at the local scale)[13]. Sulfur K-edge spectra were normalized following standard procedures and modeled by linear combinations using the Athena package [14].

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**Figure 1.** Quick S K-edge μXANES spectra for the rhyolitic ash, as compared to 4 models of S (bottom). Inset: S K-edge for various sulfates, showing the increase in the S K-edge width with distortion and polymerization, promoting feature “*” (see also [11]).

**Figure 2.** Surface-dependant quick S K-edge μXANES spectra for estimating surface speciation of S onto the rhyolitic ash (fluorescence versus total electron yield, « FLUO » and « TEY », respectively), as compared to 4 model compounds of S (bottom).
The non-normalized S K-edge XANES spectra were used to derive an estimate on the S-concentration on the sample surface. Relative to barite and chalcopyrite, the glasses of silica, rhyolite, andesite and dacite composition show 0.1, 0.7, 0.4 and 1.0 wt.% S sorbed onto their surface, respectively.

2. Results

Figure 1 shows the evolution of photoreduction on the normalized sulfur K-edge-, quick-, μXANES spectra for the rhyolite sample and 4 selected model compounds of sulfur: iron-copper sulfide (chalcopyrite), native sulfur (α phase), Na-bisulfite and barium sulfate (barytine). The inset in Figure 1 shows the variation of the S K-edge among sulfates [11]. The increase in edge width for sulfates is related to the high valence of S which promotes a strong radial distortion around the sulfate moieties in the lack of network modifiers (weakly bonded cations) around S, as observed also for Cr (CrO₃ versus chromates)[13]. Therefore, the feature “*” near 2479 eV can also be related to sulfate distortion whereas those near 2477 eV are related to local bondings involving S(IV)–S(V) species (see [4,6-9]).

The quick μXANES spectra for the rhyolite ash are dominated by a signal arising from sulfate-type moieties near 2482 eV. Photoreduction promotes the presence of “reduced” species of sulfur, which absorption edges are located below 2480 eV. However, S-species related to S(IV) are yet observable at very low irradiation times (below 20 sec) and their presence is greatly enhanced for higher irradiation times. Therefore, this suggests that some reduced species of S were also possibly sorbed on the glass surface (together with major amounts of sulfates) but they were greatly enhanced by photoreduction.

Figure 2 shows that photoreduction is also enhanced on the few nanometers of the sample surface as the normalized TEY signal for reduced species of S is more intense as compared to its fluorescence counterpart, even after 120 seconds of beamtime exposure. As for thionates [7], the peak for the bridging S (S-S) for the rhyolite surface is slightly shifted to higher energies as compared to native α-S.

Figure 3 shows normalized spectra (average of 4-10 points, quick-XANES, no more than 25 seconds irradiation time for each point) for the four glasses, as compared to quartz. Quartz does not show any significant amount of adsorbed sulfur. In contrast glassy silica show lots of...
adsorbed S, like the 3 volcanic glasses (andesite, dacite and rhyolite). The S-speciation differs slightly on glass composition. The volcanic compositions show the highest percentage of sulfates whereas silica show significantly more reduced species. Linear combinations of the XANES spectra show that sulfates represent 71, 64 and 49 atom% (of the total S, ± 5), in rhyolite, dacite and andesite respectively. Sulfite-type species represent 21, 22 and 30 % while (S-S) bridges are 8, 14 and 21 %.

Figure 4 shows a μXRF map of the Kα fluorescence of S for rhyolite. The map highlights the heterogeneous distribution of S on the sample, with “hot spots” of S (see “spot 1” on Figure 3) over a more homogeneous distribution of S (“background S”; see “spot 2” on Figure 3). Both locations show distinct speciation: the “hot spot” shows less sulfates and more reduced species.

3. Discussion

On those glass surfaces, sulfur is present mostly as sulfate moieties. Reduced species of S are also observed: S(IV)-type species, S-bridges related to S(0 ± 0.5) and weak amounts of sulfide-type environments. Most of those species are not related to photoreduction artifacts but the presence of S(IV)-type species on the glass surface is not excluded, related to a “direct sorption” of SO2. When photoreduction is minimized as much as possible, the presence of reduced species of sulfur is more related to S-rich regions, whereas sulfates are more representative of the “background”. The surface structure controls the sorption of S. While crystalline quartz does not adsorb any S, vitreous silica does. But volcanic glasses are even better glassy substrates to adsorb S. Therefore, both the presence of surface defects (glass versus crystal) and network modifiers (alkali and alkali-earths) are important for S to bond onto the ash surface, whereas bulk glass polymerization does not seem to be as critical (NBO/T, the non-bridging oxygen per tetrahedron ration, ranging from 0.0 in silica to 0.6 in andesite).

Although little is known on the exact structure of glass nanosurfaces, surface relaxation is likely to occur, especially around bridging oxygens. Then, polymerization is likely to decrease on the glass surface (as compared to the bulk). Sulfates moieties require weakly bonded network modifiers to be stabilized (due to the high valence of S in those species). Therefore, sulfates are more prompt to be adsorbed on volcanic glass compositions because their surface can provide reactive alkali and alkali-earth cations to charge-compensate S(VI). S(IV)-type species are possibly “relicts” of the original SO2 which reacted primarily on the glass surface before most of that S would oxidize into S(VI). Because sulfates are formed on glasses and not on quartz, volcanic ashes are likely to adsorb major quantities of S in their glassy microregions. Since SO2 is oxidized to sulfate on the ash surface, the adsorption process is largely irreversible. Adsorption of SO2 on ashes in the volcanic plume is an important process that needs to be considered in models of the impact of volcanic eruptions on climate.

4. References

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