

The origin of S⁴⁺ detected in silicate glasses by XANES

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ABSTRACT

The origin of sulfite (S⁴⁺) species in silicate glasses was evaluated using XANES at the S *K*-edge. Systematic investigations show that the presence of S⁴⁺ species in silicate glasses is an analytical artifact related to changes in the sulfur species caused by irradiation with an electron beam during EMPA or by irradiation with an intense focused X-ray beam during synchrotron analysis. The data shown here indicate that S²⁻ and S⁶⁺ are the only significant sulfur species occurring in silicate glasses synthesized under geologically relevant conditions.

Keywords: XAS (XAFS, XANES), sulfur *K*-edge, glass properties, sulfur oxidation state, beam damage, sulfur speciation

INTRODUCTION

Although sulfur is typically a trace element in silicate melts (rarely more than 5000 ppm) it is an important element in magmatic processes for two main reasons. First, sulfur (as sulfide) controls the behavior of several metals of economic or petrogenetic interest in silicate melts. Second, explosive volcanic events are capable of releasing large amounts of sulfur (as SO₂) into the atmosphere, significantly affecting global climate (Self et al. 1996). Sulfur is also important in industrial processes, particularly in the production of technical glasses. Sulfur compounds are used during glass refinement in the removal of bubbles and impurities from the melt (Beerkens 2003; Beerkens and Kahl 2002). Knowledge on the sulfur budget and dissolution mechanism helps to improve this process. Industrial control of S content and speciation is also important in the manufacturing of colored glass (especially amber-colored glass), which is a key feature in several end-products (Beerkens 2003; Müller et al. 1999).

The S redox equilibrium is usually described considering only S²⁻ and S⁶⁺ species in the melt (Fincham and Richardson 1954):



Experiments have shown that the amount of S that can be dissolved in silicate melts is controlled by the nature of the satu-

rating phase and that S contents at saturation are usually much higher when S is present as sulfate (S⁶⁺) than when S is present as sulfide (S²⁻) (Carroll and Rutherford 1985, 1987; Luhr 1990; Jugo et al. 2005a). This change in S speciation occurs over a range of *f*_{O₂} (from FMQ to about FMQ+2) that is relevant for the formation of magmas (Wallace and Carmichael 1992; Jugo et al. 2005b). For example, S speciation in rifting-related magmas is dominated by S²⁻, as evidenced by measurements on submarine glasses (Wallace and Carmichael 1992, 1994), whereas arc-related magmas more often show the presence of S⁶⁺ in melt inclusions found in olivine and amphibole (Métrich et al. 2002; De Hoog et al. 2004; Rowe et al. 2007).

Investigations on the sulfur oxidation state in quenched melts using electron microprobe analysis (EMPA) and the wavelength shift of the SK α emission peak (Carroll and Rutherford 1988; Wallace and Carmichael 1994; Jugo et al. 2005b; Rowe et al. 2007) is based on the assumption that only S²⁻ and S⁶⁺ species are present. This technique cannot determine directly the presence of any sulfur species in silicate melts and relies on comparisons to the wavelength of the SK α emission peak of crystalline standards (e.g., barite and sphalerite). In contrast, the fine structure found in X-ray absorption near edge structure (XANES) is related to 1s–3p electronic transitions that are sensitive to the electronic configuration and thus, provide insight to the chemical state of S in the sample (Li et al. 1995; Fleet 2005). Métrich et al. (2002) and Bonnin-Mosbah et al. (2002) documented the presence of S⁴⁺ in natural melt inclusions in olivine of arc-related magmas, in addition to S⁶⁺ and, to a minor extent, S²⁻. In both studies a strongly focused X-ray beam was used. Métrich et al. (2002) suggested that the potential existence of a third sulfur species in magmas would have significant implications for the processes

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occurring during degassing of magmas. This would also imply that the oxidation of sulfide to sulfate in silicate melts follows a two-step reaction mechanism with sulfite as intermediate species in the transition from sulfide to sulfate.

Compilation of the data obtained by wavelength shift of the SK α emission peak (Jugo et al. 2005b) shows a significant difference in the wavelength measured on oxidized glasses relative to the sulfate standard (e.g., barite). The nature of this difference is consistent with the presence of another sulfur species such as S⁴⁺ (sulfite) as proposed by Métrich et al. (2002). However, another possibility for the presence of S⁴⁺ in the XANES spectra (and for the difference of the wavelength of the SK α emission peak in EMPA) is that interaction of the intense focused X-ray beam or the electron beam with the sample during the analysis causes changes in the S speciation. The occurrence of such beam damage has been documented in studies of heterovalent elements on organic or biological materials (Jäger et al. 1997; Kanngiesser et al. 2004). Changes in the speciation by the beam may even be a problem for studies on crystalline and amorphous silicate phases, depending on the intensity of the beam (Shimizugawa et al. 2001; Eeckhout et al. 2005). Fleet et al. (2005) noted already that the spectral presence of S⁴⁺ in glass might be related to auto-redox reactions at/near the sample surface during either sample preparation or XANES measurement. In this communication, we provide XANES spectra showing that S⁴⁺ present in quenched glasses and documented in XANES analysis is related to speciation changes produced either during the EMPA or during the acquisition of XANES spectra, particularly when using an intense focused X-ray beam.

EXPERIMENTAL METHODS

XANES spectra were collected at the European Synchrotron Radiation Facility (ESRF), Grenoble, France at the micro-focus beamline ID21 and at the Swiss Light Source (SLS), Villigen, Switzerland at the LUCIA beamline. At both beamlines, Si(111) double-crystal monochromators were used. The spectra were collected in fluorescence mode using energy dispersive Si-drift chamber solid-state detectors. Higher harmonics in the incident beam were rejected using two plane-parallel mirrors with an adjustable angle of incidence. The incident beam intensity was measured using a photodiode. At the ESRF, the beam was either collimated using a pin hole to a beamsize of 200 μm in diameter or focused using a zone plate that provided a spot size of 0.5 to 0.8 μm in diameter. At the SLS, the beam was focused down to 3 μm in diameter with two mirrors in a Kirkpatrick-Baez arrangement.

The XANES spectra were collected from 2450 to 2550 eV. At the ESRF, the spectra were acquired by continuously scanning the monochromator and the gap of the undulator, resulting in a sampling step size of 0.23 eV. These quick-scans were stacked until an appropriate signal-to-noise ratio was achieved. At the SLS, spectra were acquired by stepwise scanning the angle of the monochromator and the gap of the undulator. Close to the S K-edge, the step size was 0.3 and 1 eV in the other energy regions (1 s acquisition time per step). Spectra were normalized by fitting the energy region before the edge using a polynomial and subtracting this as background. The edge-jump was normalized to unity by fitting an arctangent and a Gaussian function to the spectra.

Results from five of the samples analyzed at the ESRF are shown. Two samples (pj034 and pj050) were taken from the studies of Jugo et al. (2005a, 2005b). These samples are basaltic and were synthesized at 1 GPa, 1300 °C at sulfate-saturated conditions. To investigate the effect of water dissolved in the glass on the occurrence of S⁴⁺, samples of andesitic composition (samples SA4 and SA28) were synthesized in an internally-heated pressure vessel at 200 MPa, 1050 °C, at sulfate-saturated conditions, and with 5 wt% total H₂O content. The composition of these andesitic samples was based on the average composition for andesite as referenced by www.earthchem.org. Finally, a disequilibrium sample of andesitic composition was synthesized in a piston-cylinder apparatus (sample pj086). This sample was produced by annealing of a sulfate-saturated glass within a graphite capsule for a short time period (60 min) at 1 GPa and 1300 °C. The enclosing graphite capsule interacts

with the silicate melt creating a reduction front that advances toward the center of the capsule progressively reducing S and causing sulfide precipitation. However, because of the short duration of the experiment, complete reduction was avoided, so that the central part of the capsule contained glass (with 3600 ppm S) coexisting with sulfate phases, and a reduction profile was preserved. In addition, results of one sample are shown that was analyzed at the SLS. This sample represents a hydrous soda lime silica glass (wt% anhydrous: SiO₂ 67.3; CaO 7.7; Na₂O 22.5) containing ca. 2 wt% of S. The sample was synthesized at 200 MPa and 1000 °C at reducing conditions (ca. QFM) with total water content of 5 wt%.

RESULTS AND DISCUSSION

Evidence for beam damage by electron microprobe analysis

Normalized XANES spectra of two samples synthesized under oxidizing conditions (samples pj034 and pj050) are shown in Figure 1a. The samples used were previously analyzed by EMPA for S content and speciation (Jugo et al. 2005a, 2005b). Only the carbon coating was removed before the XANES measurement. The spectra shown were taken randomly on several areas of the samples using an unfocused, collimated beam. Some areas analyzed by XANES in these samples had been irradiated previously by the electron beam during EMPA. The strong peak at 2482.5 eV indicates that S⁶⁺ is the dominant species in these samples. In addition, a peak at ca. 2478.5 eV with variable intensity in height from point to point can be observed. This peak is related to S⁴⁺ as shown by measurements on model-compounds (Li et al. 1995; Bonnin-Mosbah et al. 2002; Métrich et al. 2002; McKeown et al. 2004; Fleet 2005). The samples were extensively re-polished after this set of measurements to provide a pristine surface and re-analyzed by XANES as before. In this case, only the strong peak at 2482.5 eV related to S⁶⁺ was observed (Fig. 1b). Thus, the presence of S⁴⁺ in the first set of measurements was likely caused by S reduction from S⁶⁺ to S⁴⁺ produced by the electron beam during EMPA.

Evidence for beam damage during XANES measurements

A comparison between XANES measurements on an anhydrous andesitic glass taken with (1) the 200 μm diameter unfocused beam, and (2) a focused beam with 0.8 μm diameter is shown in Figure 2a. The spectrum taken with the unfocused beam shows only the peak related to sulfate, whereas the spectrum taken in focused mode (on the same area) provides clear evidence for the presence of S⁴⁺ and a decrease in the intensity of the S⁶⁺ peak. Because spectra were taken by stacking of quick-scans, the formation of S⁴⁺ during the measurements can be observed by comparing sequences of individual quick-scans. The average of the first two and the last two quick-scans of a total of 40 scans are shown in Figure 2b. These two spectra clearly highlight the intensity increase of the 2478.5 eV peak during the measurement. These changes are likely caused by S reduction induced by the photon beam during XANES analysis.

Spectra taken on oxidized hydrous andesitic glasses containing ca. 5 wt% water and 1900/2850 ppm S (samples SA4 and SA28) are shown in Figure 3a. The spectra shown refer to replicate measurements using an unfocused beam on one spot with an acquisition time of ca. 40 min each. In one measurement (SA28 spot 1-2), a small but significant change around 2478.5 eV was recorded, whereas no significant change is observed in the measurements of SA4. SA4 1-1, however, looks already similar to SA28 1-2. These two examples may indicate that for

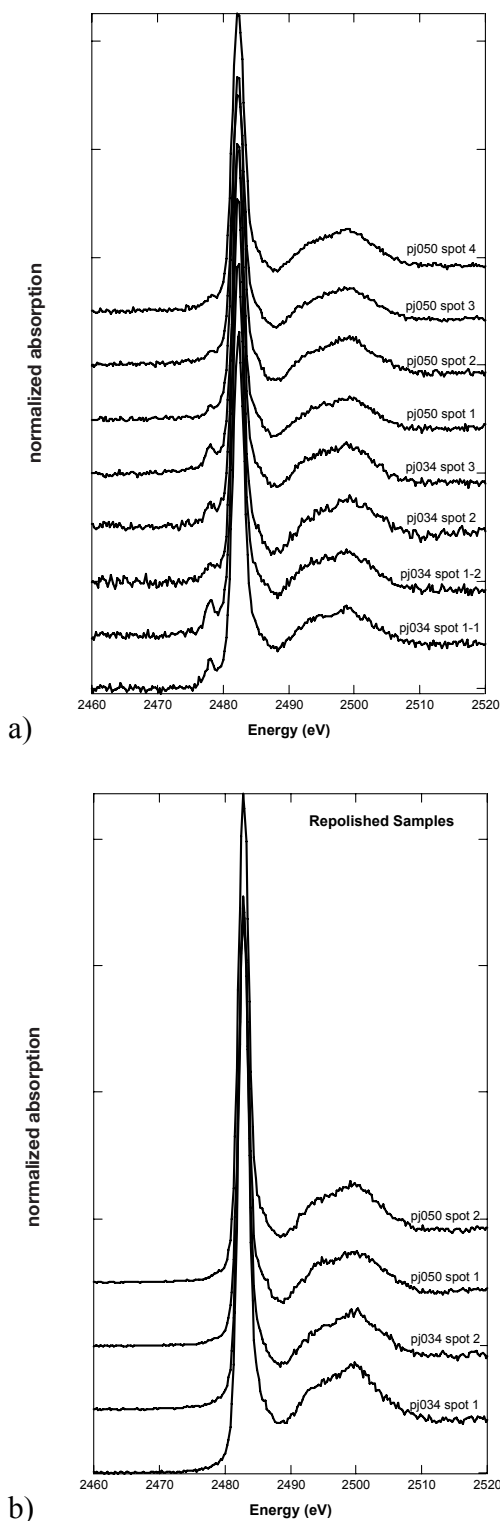


FIGURE 1. (a) Normalized XANES spectra at the S K-edge measured on several spots of samples pj034 and pj050 (taken from Jugo et al. 2005a, 2005b: no. 34, no. 50). Samples were analyzed by electron microprobe before the XANES measurements. (b) Normalized XANES Spectra at the S K-edge measured of the same samples after re-polishing of the sample surface.

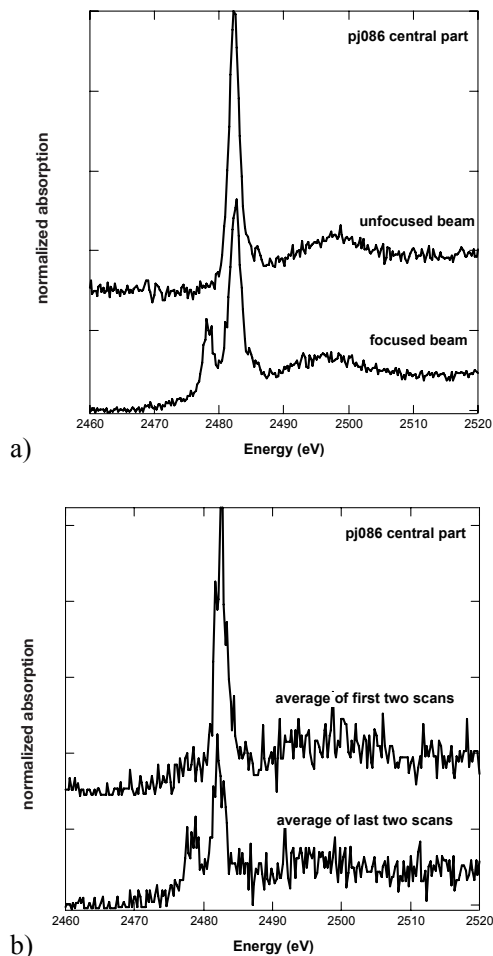


FIGURE 2. (a) Comparison of normalized XANES spectra taken in the central area of sample pj086 (disequilibrium sample, sulfate-saturated part) with unfocused (200 μm) and focused (0.8 μm) excitation beams. (b) Comparison of initial (sum of the quick scans 1 and 2) and final scans (sum of quick scan 39 and 40) that were accumulated for the focused-beam spectrum (lower spectrum in a).

hydrous glasses beam damage might be even a problem when using an unfocused beam.

A series of spectra were taken at the SLS on a partly reduced hydrous NaCa-silica glass. The first spectrum (Cycle 1 in Fig. 3b) was obtained by constantly moving the sample in the beam at a rate of $\sim 100 \mu\text{m/s}$. Four peaks are present in this spectrum: one related to S⁶⁺ (at 2482.5 eV); two related to S²⁻, a broad one centered at about 2476 eV and a sharp one at 2472 eV (McKeown et al. 2004; Fleet 2005); and one at 2466 eV, which to our knowledge has not been documented in model compounds, yet. However, despite the coexistence of peaks related to the existence of S⁶⁺ and S²⁻ species, the peak related to S⁴⁺ (at ~ 2478.5 eV) is not present, as would be expected if the oxidation of S²⁻ to S⁶⁺ required the presence of intermediate species as suggested by Métrich et al. (2002) and Bonnin-Mosbah (2002). Additional spectra, obtained at a fixed sample position (Cycles 2 to 7, Fig. 3b) show the appearance of a S⁴⁺ peak at ~ 2478.5 eV. In addition, the peak at ~ 2472 eV (indicative for S²⁻ as observed

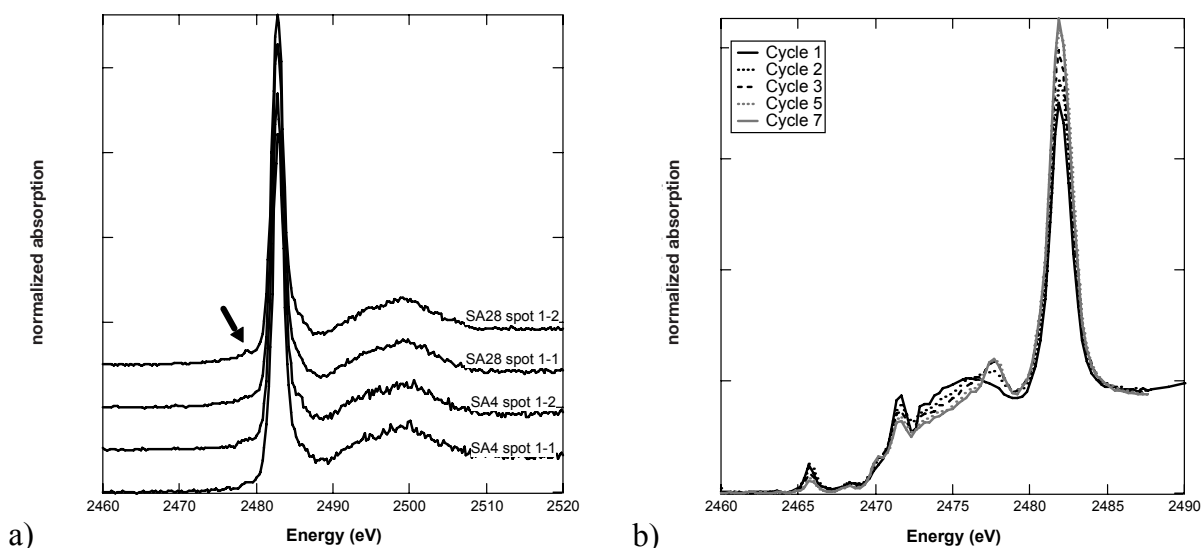


FIGURE 3. (a) Normalized XANES Spectra at the S *K*-edge measured on two oxidized hydrous andesitic glasses (SA4 and SA28) with an unfocused beam as indicated. The two spectra shown for each sample correspond to replicate measurements at the same spot (acquisition time 40 min for each measurement). (b) Normalized XANES spectra measured on a partially reduced hydrous NaCa-silicate glass using a focused beam for excitation (taken at SLS). During Cycle 1, the sample was constantly moved under the beam. Cycles 2 to 7 correspond to replicate measurements on a single spot.

in monosulfides; Fleet 2005) decreased and the peak for S⁶⁺ at 2482.5 eV increased. In contrast to the decrease of the peak at 2472 eV, a feature at ca. 2470 eV emerges in Cycles 2–7, which is also related to sulfide (Fleet 2005; McKeown et al. 2004). The formation of S⁴⁺ is relatively quick and a maximum peak height is observed after the 3rd cycle (corresponding to ~150 s). The decrease of S²⁻ (2472 eV) and the increase of S⁶⁺ (2482.5 eV) have not shown a maximum, so far. The changes observed with time indicate an apparent oxidation through the formation of S⁴⁺ and the increase of S⁶⁺. This behavior is essentially the opposite of the photo-reduction observed during XANES analysis at the ESRF. At the ESRF, spectra taken on partially or completely reduced glasses (dry and hydrous) have not shown any evidence for changes in the sulfur speciation. We are not certain about the causes of this discrepancy but we suggest that the processes occurring during irradiation might be more complex than just oxidation or reduction of S species. This is indicated by the increase of the feature around 2470 eV for the SLS spectra. The change at this position may also point to a re-organization of the local structural environment. The position and intensity of this feature is sensitive to the nearest neighbors of S²⁻ as observed for crystalline sulfides (Fleet 2005; McKeown et al. 2004). The different behavior for the measurements at the ESRF and SLS are probably related to the difference in intensity of the two experimental setups and/or of the glass chemistry.

Sulfur species found in disequilibrium sample

An additional test for the potential presence of S⁴⁺ was performed on samples synthesized under disequilibrium conditions. As mentioned before, these samples contain sulfate-bearing andesitic glass in the central part, which is reduced to sulfide-bearing glass at the rim. The purpose of these experiments was to preserve the gradual change of the sulfur species in the glass

from the center to the rim of the sample. Thus, if S⁴⁺ is a stable species in melt and the intermediate species in the transition from S²⁻ to S⁶⁺ then it should be present along the reduction profile from the rim to the center of the sample. Point analyses by XANES using a focused beam are not possible without changing the sulfur species as shown before. Instead, we performed scans across the sample using several different energies for excitation. In this way the photon dose on the sample is minimized, reducing the influence of the beam on the analysis. The excitation energies were chosen at positions of resonances of the possible sulfur species S²⁻, S⁴⁺, and S⁶⁺ and at energies below the edge and above the edge for normalization as indicated in Figure 4a. The energies chosen were 2476.5 eV for S²⁻ in glass according to the measurement on a reduced basaltic glass, 2478.5 eV for S⁴⁺ as measured on sodium sulfite (see also Métrich et al. 2002; Fleet 2005), and 2482.5 eV for S⁶⁺ as measured on sulfate minerals and on oxidized glasses. Finally, 2460 and 2515 eV were used for background correction and edge-jump normalization. The normalized intensity for each energy as a function of the position on the sample is shown in Figure 4b. The signal related to S⁶⁺ starts to increase at ca. 20 μm and reaches its maximum level at ca. 100 μm. The signal related to S²⁻ has its maximum level close to the sulfide bleb and starts to decrease at ca. 10 μm from the rim. The signal at 2478.5 eV (S⁴⁺) is similar in height as the one at 2476.5 eV (S²⁻) from close to the rim up to 40 μm. The resonance that can be related to S⁴⁺ is usually sharp and intense (McKeown et al. 2004; Fleet 2005). Therefore, any significant presence of S⁴⁺ would lead to a strong increase of the signal at 2478.5 in comparison to the one at 2476.5 eV. Only in the region close to the center does it exceed the one at 2476.5 eV, but this is related to contributions by the strong S⁶⁺ peak. Thus, these data also indicate that S²⁻ and S⁶⁺ are the only sulfur species that are present and that may coexist in silicate glasses.

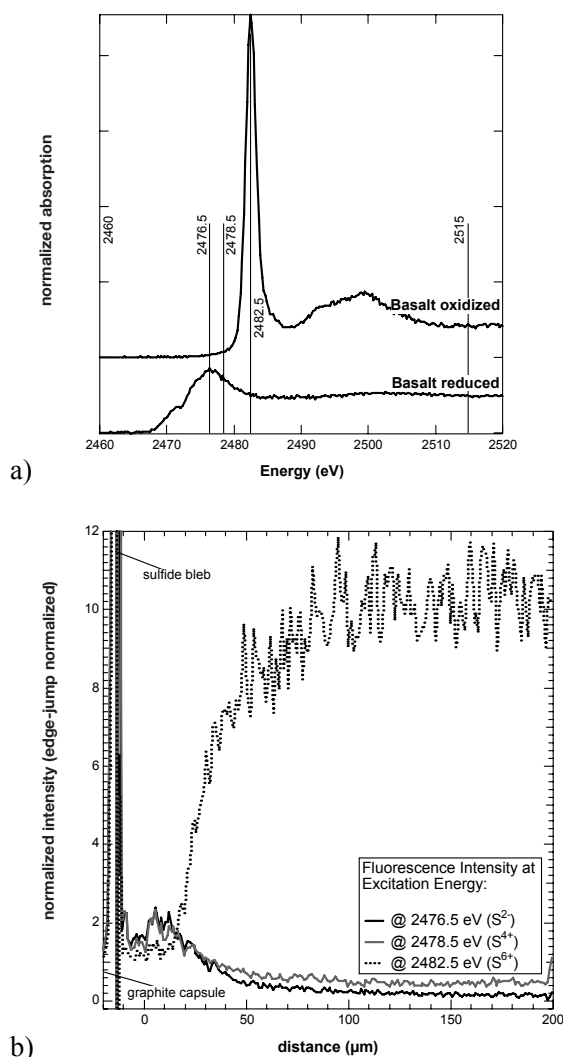


FIGURE 4. (a) Normalized XANES of S in basaltic glasses synthesized at 1 GPa, 1300 °C under oxidizing and reducing conditions. Spectra are representative for S⁶⁺ and S²⁻ in silicate glasses and define the excitation energies (shown in vertical lines) that were used in the energy scans along the reduction-front in sample pj086. Note that in samples containing only S²⁻ there will be also a significant background signal at the positions of the other species. (b) Normalized sulfur K- α fluorescence intensities excited at the energies indicated as a function of distance along the reduction profile. Intensity recorded at 2476.5 eV corresponds to preferential excitation of S²⁻ in glass, intensity at 2478.5 eV to S⁴⁺, and intensity at 2482.5 eV to S⁶⁺. The zero in the distance scale is arbitrary and related to the absolute position of the sample stage. The left margin of the plot corresponds to the edge of the graphite capsule.

Our results strongly indicate that only S²⁻ and S⁶⁺ coexist in silicate glasses and that S⁴⁺ is not a stable species. Our data show that formation of S⁴⁺ occurs during sample irradiation with electron beams or intense X-ray beams. During EMPA beam-sample interaction causes reduction of S⁶⁺ species to S⁴⁺, especially during determinations of wavelength shifts of the SK α , which require relatively long counting times (typically more than 10 min). This beam damage affects the determination

of the proportion of S species by wavelength shifts and explains why non-linear regressions of EMPA data on S speciation do not converge to the theoretical values (i.e., 100% S⁶⁺ in oxidized samples) as documented in Jugo et al. (2005b). The wavelength shift of the SK α emission toward the one of the sulfate standard during long EMPA has been interpreted as oxidation of the sulfur in the glass (Wallace and Carmichael 1994; Rowe et al. 2007). Our results strongly indicate that this interpretation may not be adequate. During analyses with an X-ray beam, the formation of S⁴⁺ is closely related to the photon dose during the measurement. However, the effect of intense X-ray beams is complex. All measurements performed at the ESRF show photo-reduction of S⁶⁺ to S⁴⁺ as the dominant process, which is consistent with other photon-induced changes especially in soft condensed matter (Jäger et al. 1997; Kanngiesser et al. 2004). In contrast, the measurements obtained at the SLS with a more intense beam, which was focused by mirror optics (ca. two orders of magnitude higher), indicate the occurrence of photo-oxidation or more complex processes. Furthermore, beam damage may also depend on the composition of the glass. The presence of water in the glass, in particular, may accelerate the reactions. In all cases, the time needed to produce significant amounts of S⁴⁺ decreased with increasing beam intensity. Still, the formation is not immediate (in the order of minutes in worst cases) and analytical protocols (such as the scans shown in Figs. 3b and 4b) can be designed to circumvent this problem.

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REFERENCES CITED

- Beerens, R.G.C. (2003) Amber chromophore formation in sulphur- and iron-containing soda-lime-silica glasses. *Glass Science and Technology*, 76, 166–175.
- Beerens, R.G.C. and Kahl, K. (2002) Sulfur chemistry in soda lime silica glass melts. *Physics and Chemistry of Glasses*, 43, 189–198.
- Bonnin-Mosbah, M., Métrich, N., Susini, J., Salome, M., Massare, D., and Menez, B. (2002) Micro X-ray absorption near edge structure at the sulfur and iron K-edges in natural silicate glasses. *Spectrochimica Acta B*, 57, 711–725.
- Carroll, M.R. and Rutherford, M.J. (1985) Sulfide and sulfate saturation in hydrous silicate melts. *Journal of Geophysical Research* 90, C601–C612.
- (1987) The stability of igneous anhydrite: Experimental results and implications for S behavior in the 1982 El Chichón trachyandesite and other evolved magmas. *Journal of Petrology*, 28, 781–801.
- (1988) Sulfur speciation in hydrous experimental glasses of varying oxidation states: Results from measured wavelength shifts of sulfur X-rays. *American Mineralogist*, 73, 845–849.
- De Hoog, J.C.M., Hattori, K.H., and Hoblitt, R.P. (2004) Oxidized sulfur-rich mafic magma at Mount Pinatubo, Philippines. *Contributions to Mineralogy and Petrology*, 146, 750–761.
- Eeckhout, S.G., Neisius, T., and Castañeda, C. (2005) Oxidation effects in beryl induced by synchrotron radiation. *Nuclear Instruments and Methods in Physics Research B*, 229, 73–77.
- Fincham, C.J.B. and Richardson, F.D. (1954) The behavior of sulfur in silicate and aluminate melts. *Philosophical Transactions of the Royal Society London*, A223, 40–62.
- Fleet, M.E. (2005) XANES spectroscopy of sulfur in earth materials. *Canadian Mineralogist*, 43, 1811–1838.
- Fleet, M.E., Liu, X., Harmer, S.L., and King, P.L. (2005) Sulfur K-edge XANES spectroscopy: Chemical state and content of sulfur in silicate glasses. *Canadian Mineralogist*, 43, 1605–1618.
- Jäger, B., Schürmann, H., Müller, H.U., Himmel, H.J., Neumann, M., Grunze, M., and Woll, C. (1997) X-ray and low-energy electron induced damage in alkane-

- thiolate monolayers on Au-substrates. *Zeitschrift für Physikalische Chemie*, 202, 263–272.
- Jugo, P.J., Luth, R.W., and Richards, J.P. (2005a) Experimental data on the speciation of sulfur as a function of oxygen fugacity in basaltic melts. *Geochimica et Cosmochimica Acta*, 69, 497–503.
- (2005b) An experimental study of the sulfur content in basaltic melts saturated with immiscible sulfide or sulfate liquids at 1300 °C and 1.0 GPa. *Journal of Petrology*, 46, 783–798.
- Kanngiesser, B., Hahn, O., Wilke, M., Nekat, B., Malzer, W., and Erko, A. (2004) Investigation of oxidation and migration processes of inorganic compounds in ink-corroded manuscripts. *Spectrochimica Acta B*, 59, 1511–1516.
- Li, D., Bancroft, G.M., Kasrai, M., Fleet, M.E., Feng, X.H., and Tan, K. (1995) S *K*- and *L*-edge X-ray absorption spectroscopy of metal sulfides and sulfates: applications in mineralogy and geochemistry. *Canadian Mineralogist*, 33, 949–960.
- Luhr, J.F. (1990) Experimental phase relations of water- and S-saturated arc magmas and the 1982 eruption of El Chich volcano. *Journal of Petrology*, 31, 1071–1114.
- McKeown, D.A., Muller, I.S., Gan, H., Pegg, I.L., and Stolte, W.C. (2004) Determination of sulfur environments in borosilicate waste glasses using X-ray absorption near-edge spectroscopy. *Journal of Non-Crystalline Solids*, 333, 74–84.
- Métrich, N., Bonnin-Mosbah, M., Susini, J., Menez, B., and Galois, L. (2002) Presence of sulfite (S^{IV}) in arc magmas: Implications for volcanic sulfur emissions. *Geophysical Research Letters*, 29, 1538, DOI: 10.1029/2001GL014607.
- Müller, M., Rüssel, C., and Claussen, O. (1999) UV-VIS spectroscopic investigations of amber glass at high temperatures. *Glastechnische Berichte Glass Science and Technology*, 72, 362–366.
- Paris, E., Giuli, G., Carroll, M.R., and Davioli, I. (2001) The valence and speciation of sulfur in glasses by X-ray absorption spectroscopy. *Canadian Mineralogist*, 39, 331–339.
- Rowe, M.C., Kent, A.J.R., and Nielsen, R.L. (2007) Determination of sulfur speciation and oxidation state of olivine hosted melt inclusions. *Chemical Geology*, 236, 303–322.
- Self, S., Zhao, J., Holasek, R.E., Torres, R.C., and King, A.J. (1996) The atmospheric impact of the 1991 Mount Pinatubo eruption. In C.G. Newhall and R.S. Punongbayan, Eds., *Fire and Mud: Eruptions and Lahars of Mount Pinatubo*, Philippines, p. 1098–1115. Philippine Institute of Volcanology and Seismology and University of Washington Press, Seattle.
- Shimizugawa, Y., Umesaki, N., Hanada, K., Sakai, I., and Qiu, J.R. (2001) X-ray induced reduction of rare earth ion doped in Na₂O-Al₂O₃-B₂O₃ glasses. *Journal of Synchrotron Radiation*, 8, 797–799.
- Wallace, P.J. and Carmichael, I.S.E. (1992) Sulfur in basaltic melts. *Geochimica et Cosmochimica Acta*, 56, 1863–1874.
- (1994) Speciation in submarine basaltic glasses as determined by measurements of SK α X-ray wavelength shifts. *American Mineralogist*, 79, 161–167.

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