

1 XANES evidence for sulphur speciation in Mn-, Ni- and  
2 W-bearing silicate melts

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## 1 ABSTRACT

S K edge XANES and Mn, W and Ni XANES and EXAFS spectra of silicate glasses synthesised at 1400° C and 1 bar with compositions in the CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-S plus MnO, NiO, or WO<sub>3</sub> systems were used to investigate sulphur speciation in silicate glasses.

S K-edge spectra comprised a composite peak with an edge between 2470 and 2471.4 eV, which was attributed to S<sup>2-</sup>, and a peak of variable height with an edge at 2480.2 to 2480.8 eV, which is consistent with the presence of S<sup>6+</sup>. The latter peak was attributed to sample oxidation during sample storage. W-rich samples produced an additional lower energy peak at 2469.8 eV that is tentatively attributed to the existence of S 3p orbitals hybridised with the W 5d states.

Deconvolution of the composite peak reveals that the composite peak for Mn-bearing samples fits well to a model that combines three Lorentzians at 2473.1, 2474.9 and 2476.2 eV with an arctan edge step. The composite peak for W-bearing samples fits well to the same combination plus an additional Lorentzian at 2469.8 eV. The ratio of the proportions of the signal accounted for by peaks at 2473.1eV and 2476.2eV correlates with Mn:Ca molar ratios, but not with W:Ca ratios. Spectra from Ni-bearing samples were qualitatively similar but S levels were too low to allow robust quantification of peak components. Some part of the signal accounted for by the 2473.1 eV peak was therefore taken to record the formation of Mn-S melt species, while the 2469.8 peak is interpreted to record the formation of W-S melt species. The 2474.9 eV and 2476.2 eV peaks were taken to be dominated by Ca-S and Mg-S interactions. However, a 1:1 relationship between peak components and specific energy transitions is not proposed. This interpretation is consistent with known features of the lower parts of the conduction band in monosulphide minerals and indicates a similarity between sulphur species in the melts and the monosulphides. S XANES spectra cannot be reproduced by a combination of the spectra of the component element monosulphides.

Mn-, W- and Ni- XANES and EXAFS for synthetic glasses without sulphide exsolution did not show any sensitivity to the presence of sulphur, which is unsurprising as S:O ratios were sufficiently low that metals would be mostly co-ordinated by O. Mn EXAFS spectra

33 were consistent with divalent Mn in 5 co-ordinated Mn-O melt species. W spectra were  
34 consistent with tetrahedrally co-ordinated hexavalent W, most likely in scheelite-like melt  
35 species, and Ni spectra were consistent with [4] co-ordinated divalent Ni. These results  
36 indicate lower coordinations for both W and Ni than those inferred by some previous workers.  
37 Cation coordination may reflect the proportion of non-bridging oxygens, which is lower in  
38 the Ca-rich and Al-poor samples investigated here than for previous studies.

## 2 INTRODUCTION

40 A quantitative understanding of the solubility of sulphur in silicate melts is necessary if we  
41 are to understand a wide range of processes that include the distribution of commercially  
42 valuable and/or geochemically significant chalcophile elements such as copper, platinum,  
43 rhenium, osmium and palladium (e.g. Naldrett, 1999; Wang and Zhou, 2006), the effects  
44 of volcanic eruptions on the atmosphere (e.g. de Hoog et al., 2004), global sulphur cycling  
45 (e.g. Alt et al., 1993; Fischer et al., 1998), and the formation of magmatic-related economic  
46 sulphide deposits (e.g. Cawthorn, 2005; Lee and Ripley, 1995; Li and Ripley, 2005; Pina et  
47 al., 2006). Quantitative understanding and predictions (e.g. O'Neill and Mavrogenes, 2002;  
48 Moretti and Ottonello, 2005) are based on the thermodynamic properties of the melts, which  
49 depend on the melt structure, which is a combination of long range structure and the short  
50 range combinations of anions and cations that are described as melt species. The term melt  
51 species is used here to describe the arrangement of the first coordination shell around the  
52 element of interest. Melt structure and speciation have historically proved difficult to identify  
53 unambiguously. This is because the temperatures at which silicate melts form are difficult  
54 to access with experiments, and because magnified atomic vibrations at high temperature  
55 induce significant deviations in the spectroscopic signal so that the results of investigations  
56 rarely provide a unique or well constrained solution. Quantification of sulphur speciation is  
57 particularly challenging because sulphur can occur in a wide range of oxidation states, from -2  
58 to +6, and because sulphur is a low atomic number element present in low concentrations in  
59 silicate melts (less than 1wt%, and often less than 0.1 wt%) which restricts the applicability  
60 of many spectroscopic techniques.

61 Methods used to derive information on the speciation of sulphur in silicate melts include  
62 relationships between the concentrations of sulphur and possible ligands such as Fe (O'Neill  
63 and Mavrogenes et al., (2002), Mn (Evans et al., 2008), and values of intensive variables such  
64 as  $fO_2$  and  $fS_2$  (e.g. Carroll and Rutherford, 1985; Fincham and Richardson, 1954; Wallace  
65 and Carmichael, 1992; Carroll and Webster, 1994; O'Neill and Mavrogenes et al., 2002) and  
66 the position of the S peak determined by electron microprobe (e.g. Carroll and Rutherford,

1988; Metrich and Clocchiati, 1996). These works have shown that sulphur concentrations are highly dependent on melt composition, particularly Fe and Mn (O'Neill and Mavrogenes et al., 2002; Evans et al., 2008), which suggests that S forms melt species with these elements. Ni partition coefficients between silicate melt and olivine (Li et al., 2003) have been used to infer the existence of a Ni-S melt species. Sulphur concentrations are also dependent on the ratio of sulphur to oxygen fugacities, and the form of this relationship indicates that sulphur dissolves as  $S^{2-}$  under reducing conditions similar to those found at mid-ocean ridges and as  $S^{6+}$  under conditions comparable to those found in the more oxidised arc volcanic environments (e.g. Metrich and Clocchiati, 1996), and that  $S^{2-}$  or  $SO_4^{2-}$  replace  $O^{2-}$  on the anion sublattice (e.g. Fincham and Richardson, 1954).

Further information on the details of sulphur speciation in silicate melts has been provided by XANES (X-ray Absorption Near edge Structure) studies (e.g. Paris et al., 2001; Bonin-Mosbah et al., 2002; Fleet, 2005; Farges et al., 2006; Wilke et al., 2008; Backnaes et al., 2008; Metrich et al., 2009). XANES uses high fluxes of monochromated light from synchrotron light sources to investigate the details of absorption edges of the elements of interest. The spectra consist of measurements of X-ray absorption by a sample as the energy of the X-rays is scanned in small steps from around 100eV below to 100 eV above the absorption edge. Variation in absorption in the vicinity of the edge are created by variation in the probabilities of the different electron transitions as a function of the incoming X-ray energy and by multiple scattering effects. These features are ultimately controlled by the immediate atomic environment of the element of interest, rather than medium or long-range ordering features, and XANES spectra have been used to determine oxidation state, site geometry, and the identity of nearest neighbours in a wide variety of materials (e.g. Li et al., 1994; Li et al., 1995; Farges et al., 1997; Berry et al., 2006; Liu et al., 2006).

XANES spectroscopy on sulphur-bearing materials of geological interest have been reviewed by Fleet et al. (2005). The sulphur K edge, which is of interest here, is attributed to the transition of S 1s electrons to unoccupied antibonding orbitals at the bottom of the conduction band. The position of the edge changes as a function of sulphur oxidation state, with up to a 12 eV difference between  $S^{2-}$  and  $S^{6+}$  (e.g. Li et al., 1995), and, to a lesser

96 extent, as a function of the electronic structure of the lower parts of the conduction bands in  
97 the materials examined. Considerable attention has been paid to the XANES spectra of the  
98 monosulfides FeS, NiS, CoS, MgS, CaS and MnS (e.g. Farrell and Fleet, 2000; Farrell and  
99 Fleet, 2001; Farrell et al., 2002). Results of this work (Fig. 1a) suggest that monosulfides  
100 that exhibit a higher degree of covalent bonding, such as FeS and CoS, have a lower energy  
101 absorption edge that results from the transition of 1s S electrons into unoccupied S 3p  $\sigma^*$   
102 orbitals hybridised with the metal 3d states. Monosulfides with bonding that has a more  
103 ionic character, such as MgS and CaS, have a slightly higher absorption edge energy because  
104 the metal 3d states are effectively unavailable for hybridisation in these materials. Spectra  
105 for solid solutions between the monosulfide end-members, where accessible, are not linear  
106 combinations of the component end-members, which indicates that electronic properties are  
107 not a linear function of sample composition. These conclusions are supported by calculated  
108 XANES spectra for the monosulfides (Soldatov et al., 2004; Kravtsova et al., 2004).

109 Most studies of XANES for sulphur-bearing silicate melts have been consistent with the  
110 presence of  $S^{2-}$  in melts from more reduced settings and  $S^{6+}$  in melts from more oxidised  
111 environments (e.g Paris et al., 2001; Fleet et al., 2005; Metrich et al., 2009). The presence of  
112 tetravalent sulphur has also been proposed on the basis of XANES spectra (Metrich et al.,  
113 2002; Bonin-Mosbah et al., 2002), but it has since been demonstrated that, in most cases,  
114 this species is an artifact of the intense microbeam used for those measurements (Wilke et  
115 al., 2008; Metrich et al., 2009). Spectra for  $S^{2-}$ -bearing natural glasses have been found  
116 to be similar to linear combinations of the XANES of sulfides of the main cations in the  
117 sample, FeS and CaS (Fleet et al., 2005). Formation of  $CaS_n$  polyhedral melt species, where  
118  $n$  is an unknown stoichiometric coefficient, was also proposed for CaS dissolved in a synthetic  
119 sodium aluminosilicate glass (Fleet et al., 2005). Metrich et al. (2009) show qualitatively  
120 that the S XANES spectra of synthetic glasses prepared under reducing conditions such that  
121 all S is present as  $S^{2-}$  are sensitive to the presence or absence of FeO. These observations lead  
122 to the hypothesis that  $S^{2-}$  in silicate melts is speciated as monosulfide-like melt species of  
123 unknown geometry and stoichiometry.

124 The aim of this study is to use XANES spectra of S in Mn-, Ni- and W-bearing syn-

125 thetic silicate glasses to investigate the hypothesis that sulphur forms monosulphide-like  
126 melt species in silicate melts. These potential ligands were chosen because of their very  
127 different effects on sulphur solubility (Evans et al., 2008). Mn strongly enhances sulphur  
128 solubility in a similar way to Fe, but has the advantage that its valence is predicted to be  
129 2+ over a wide  $f(O)_2$  range, so coupled changes in Mn and S valence during cooling are  
130 effectively precluded. Ni at low ppm concentrations causes saturation of the melt with an  
131 immiscible NiS phase, and W has little effect on S solubility, which suggests that formation  
132 of W-S melt species is limited. Observation of S speciation of melts that contain these three  
133 metals should therefore cover a wide range of melt speciation types. XANES and EXAFS  
134 (Extended X-ray Absorption Fine Structure) spectra for Mn, Ni and W were also measured  
135 to enable a complementary study of the speciation of these metals.

### 136 3 METHODS

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#### 139 3.1 Preparation of synthetic glasses

140 Preparation methods are described in detail by Evans et al. (2008a). However, brief details  
141 are provided here. Sample compositions were based on a CMAS (CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>)  
142 anorthite-diopside eutectic mix with added CaO. The Ca was added to increase the base level  
143 S concentration in the samples, which reduces analytical uncertainties. This mix is referred  
144 to here as CMAS. A number of samples were prepared with zero additive metal content  
145 to establish the baseline S XANES for the study. Comparison of these samples allows the  
146 repeatability of runs at identical, theoretically, imposed  $fO_2$  and  $fS_2$  values to be assessed.  
147 Oxides of Mn, Ni and W were added to the dried oxides and carbonates of Ca, Mg, Al and  
148 Si in concentrations that varied from 0.1 wt % to 10 wt%. The exception is run B070406,  
149 which contained Ni at 10, 15, 20, 25 and 30 wt %. Sample notation is of the form Bxxxxxy,

150 where *xxxxxx* indicates the date of the run, and *y* indicates the sample number from that  
151 run.

152 The glasses were synthesised in vertical muffle tube furnaces which have been modified  
153 to allow accurately measured gas mixes to flow upwards through the furnace. All runs were  
154 equilibrated at 1400°C.  $f\text{O}_2$  and  $f\text{S}_2$  were controlled by the proportions of CO, CO<sub>2</sub> and  
155 SO<sub>2</sub>, which were supplied to the furnace by Tylan F2800 mass flow controllers. Values of  
156  $f\text{O}_2$  and  $f\text{S}_2$  corresponding to the input gas mixes were calculated as described by O'Neill  
157 and Mavrogenes (2002). Uncertainties in  $f\text{O}_2$  and  $f\text{S}_2$  are estimated to be  $\pm 0.05$  log units  
158 (c.f. O'Neill and Mavrogenes, 2002). Samples were run for 24 hours. Previous work (O'Neill  
159 and Mavrogenes, 2002) suggests that this time is sufficient for equilibration between the glass  
160 and the input gases even when immiscible sulphide melts are formed. After 24 hours the runs  
161 were quenched by release of the melt beads into water so quench was close to instantaneous.  
162 Such a fast quench should be sufficient to preserve the composition of the melt at 1400°C,  
163 with respect to sulphur content, and to preserve melt speciation and structure at the melt-  
164 glass transition. However, it is possible that electron exchange continues down to room  
165 temperature. Most of the experiments were performed at an  $f\text{O}_2$  of -9.6 ( $\Delta\text{QFM}=-3.2$ ) and  
166 a log  $f\text{S}_2$  of -1.91. These conditions have the advantage that they produce high S contents (>  
167 0.2 wt % in most cases) without any risk of blocking the furnace with precipitated elemental  
168 S. A small number of experiments were performed at more oxidising conditions but sulphur  
169 has previously been shown to be present as S<sup>2-</sup> in the melt for all the conditions investigated  
170 here (O'Neill and Mavrogenes, 2002) except those of B190606 ( $\Delta\text{QFM}=3.4$ ). Run conditions  
171 for runs that produced data used here are summarised in Table 1.

172 Glass products were split into portions for electron microprobe and synchrotron analysis.  
173 Samples for synchrotron analysis were placed into polyethylene containers and stored. The  
174 glass beads were kept whole as far as possible, but some disintegrated somewhat during  
175 quench and the sample splitting process. Samples for probe analysis were set in EPO-FIX  
176 epoxy and polished. These samples were then examined optically for evidence of exsolution  
177 of immiscible sulphide and silicate crystal phases. The epoxy-mounted samples were then  
178 carbon-coated and analysed for major elements plus S, Mn, W and Ni on the Cameca SX100



179 electron microprobe at the Research School of Earth Sciences at the Australian National  
180 University. WDS analysis and a 15 KeV accelerating voltage was used for all elements.  
181 Raw counts were converted to element weight percentages using a modified ZAF correction  
182 scheme. The major elements were analysed first using a 10 nA, 15 KeV beam with a 10  
183 micron radius. Sulphur, Mn, W and Ni were subsequently analysed using a 100 nA, 20  
184 micron beam. Details of the sulphur measurement routine, standards, detection limits and  
185 uncertainties are provided by Evans et al. (2008a). Time series by O'Neill and Mavrogenes  
186 (2002) suggest that the length of experiment utilised here is sufficient for equilibrium to be  
187 reached, and the good repeatability of the chemical compositions between runs for this study  
188 (Evans et al., 2008) supports this conclusion. However, additional tests for equilibrium were  
189 also made in the form of multiple measurements spatially distributed over the glass surface.  
190 Samples showing variation in excess of 2% relative to the mean value were discarded.

### 191 **3.2 XAS analysis**

192 Experimental glass products designated for XANES analysis were dried, where necessary, and  
193 stored in glass tubes. The material was taken to the 1.5 GeV NSRRC (National Synchrotron  
194 Radiation Research Centre) in Hsinchu, Taiwan, which operates in a 300 mA top-up mode.  
195 Sulphur K-edge spectra were measured on BL16A (Dann et al., 1998). This beamline uses a  
196 water-cooled Si(111) monochromator to provide monochromated X-rays in the energy range  
197 2000 - 8000 eV. The monochromator energy resolution in the vicinity of S K-edge (2472  
198 eV) is 0.5 eV. Photon flux is a maximum of  $3 \times 10^{11}$  photons over an area around  $4 \times 2$   
199 mm. K-edge spectra for Mn, W and Ni were measured on BL17C. This beamline is provided  
200 with photons by a wiggler with 20cm period magnets, and energy is monochromated with a  
201 Si(111) double crystal monochromator in the range 4 - 15 KeV. Photon flux is  $10^9$  to  $10^{10}$   
202 photons per second over an area approximately  $8 \times 3$ mm, and the resolution at the Mn K, Ni  
203 K and W L3 edges is around 1 eV.

205 Glasses and standards were prepared for synchrotron analysis by crushing in an agate mortar  
206 under acetone. Crushing was employed to increase sample surface area, expose fresh surfaces  
207 for analysis, and decrease the likelihood of data artifacts as a result of self-absorption. Epoxy-  
208 mounted samples could not be used for the XANES because of the high S content of epoxy  
209 relative to the samples. Calculated absorption lengths, which is the length over which the  
210 proportion of penetrating X-ray drops by a factor of  $e$ , were 5-7 microns. The crushed  
211 material was applied onto S-free kapton tape with a paintbrush. The agate mortar and  
212 paintbrush was cleaned thoroughly after each sample was loaded, then re-used. Sample  
213 preparation blanks were undertaken by going through all the preparation steps without any  
214 sample in the agate mortar. Cl-XANES spectra measured for the sample preparation blanks  
215 (Evans et al., 2008b) did not show a signal so cross-contamination between samples is likely  
216 to have been negligible. S-XANES was measured for sample-free tape and was found to  
217 be free of any sulphur signal. Four samples at a time were loaded onto the sample holder  
218 and introduced into the sample chamber. The sample chamber was purged with helium  
219 for at least an hour after the sample introduction to remove air introduced during sample  
220 loading. The beam upstream of the sample chamber is contained within a helium-filled tube,  
221 to minimise X-ray absorption by the air. S K edge spectra were measured in fluorescence  
222 geometry, with the sample at 45 degrees to the beam. The fluorescent signal was detected  
223 using the in-house Lytle detector. The energy calibration was checked daily with a Mo foil  
224 (L3 edge: 2520 eV). Shifts in the monochromator energy were always less than 0.05 eV.

225 The XANES measurement routine consisted of 1eV, 2 second measurement steps from  
226 2272 to 2442 eV, 0.2 eV, 2 second measurements in the S K edge XANES region from 2442  
227 eV to 2502 eV, and 2 eV, 2 second measurements in the post edge region from 2502 eV  
228 to 2847 eV. Passage of the scan over the Cl edge at 2822 eV provided a useful test for  
229 contamination from epoxy or other factors as the samples were nominally Cl-free. Scans  
230 were repeated three times and averaged to optimise signal quality. Total sample collection  
231 time was around three hours for each sample.

Standards investigated included MnS, NiS (millerite), WS<sub>2</sub>, NiSO<sub>4</sub>, CaSO<sub>4</sub>, MnSO<sub>4</sub>, FeS and FeS<sub>2</sub>. The MnS was sourced from a new container of synthetic MnS from Sigma Aldrich (99% pure). This container was opened for the first time at the beamline on the day of the standard analysis. Millerite and pyrite were taken from natural samples provided by the mineral collection at the Department of Earth and Marine Sciences at the Australian National University. Other standards were taken from the existing chemical collection at the Research School of Earth Sciences, Australian National University. All standards except the MnS were checked with X-ray diffraction prior to the synchrotron experiment. Results were analysed with Siroquant (Taylor, 1991) and contaminants were not detected. It was not possible to measure spectra for CaS and MgS standards because of the extreme tendency of these phases to oxidise on contact with air, which necessitates glove-box facilities for sample insertion. Such facilities were not available at the NSRRC beamline. Instead, spectra were obtained by digitisation of published spectra from Farrell and Fleet (2000). These spectra were aligned with XANES measured for this work by comparison of acquired FeS spectra with digitised FeS spectra from Farrell and Fleet (2000).

The potential for oxidation during sample preparation was investigated because sulphur is susceptible to preparation-induced oxidation (Fleet, 2005). Two subsamples from four of the glass beads were prepared (a) by grinding under acetone in air and (b) by grinding under acetone in a nitrogen-filled glove box. XANES spectra for the two sub-samples were then compared.

### 3.2.2 Mn, W and Ni analysis

Standards analysed included Mn, Ni, and W metals, MnO, MnO<sub>2</sub>, MnS, WS<sub>2</sub>, WO<sub>3</sub>, CaWO<sub>4</sub> (scheelite), NiS (millerite) and NiO. The metal standards were foils provided by the beamline. MnO, MnO<sub>2</sub>, MnS and WS<sub>2</sub> were 99% pure or better commercial powders from Sigma-Aldrich. Spectra for the MnO, MnO<sub>2</sub>, MnS and WS<sub>2</sub> were taken on the same day that the containers, previously sealed by the manufacturers, were opened. CaWO<sub>4</sub> was a natural scheelite; the sample was checked by XRD and found to be >99% pure scheelite. WO<sub>3</sub> and

259 NiO were >99% pure powders purchased from Sigma-Aldrich. NiS was a natural millerite  
260 sample; the identity and purity of the material were confirmed by XRD.

261 The monochromator energy was calibrated using the metal foils. The first derivative of  
262 the Mn K edge, W L3 edge and Ni K edge were set to 6539, 8333 and 10207 eV respectively  
263 prior to analysis for each of these metals. All standards except for the pure metals were  
264 powdered under acetone in an agate pestle and mortar and applied to kapton tape with a  
265 paintbrush. Standard analysis utilised the transmitted signal, to avoid problems with self  
266 absorption.

267 Metal XANES and EXAFS measurements on the samples were performed on either  
268 crushed sample applied to tape, as described above for the S K edge measurements, or  
269 on the polished sample fragments set in epoxy that were used for the electron microprobe  
270 analysis. In the latter case, flexible lead sheet was used to shield the parts of the mount that  
271 did not contain the sample under investigation. No systematic difference in sample spectra  
272 were noted as a result of the two different sample preparation methods. Sample analysis  
273 utilised the fluorescence signal.

274 Scans across the Mn K-edge were measured for 2 seconds per point in 7 eV steps between  
275 200 and 25eV below the edge, for 2 seconds per point in 0.3 eV steps in the XANES region  
276 from 25eV below to 50 eV above the edge, and for 4 seconds per point in 0.06  $k$  unit steps  
277 in the EXAFS region from 50 to 540eV above the edge.  $k$  is the relative wave number  
278 of the photo-electron ejected in the absorption process, and is related to energy by  $k^2 =$   
279  $2m_e(E - E_0)/\hbar^2$ , where  $m_e$  is the mass of an electron,  $E$  and  $E_0$  are the energy and edge  
280 energy respectively, and  $\hbar$  is the reduced Planck's constant.

281 Scans across the W L3 edge were measured for 2 seconds per point in 7.5 eV steps between  
282 200 and 20eV below the edge, for 2 seconds per point in 0.4 eV steps in the XANES region  
283 from 20eV below to 40 eV above the edge, and for 2 seconds per point in 0.06  $k$  unit steps  
284 in the EXAFS region from 80 to 1000eV above the edge.

285 Scans across the Ni K edge were measured for 2 seconds per point in 10 eV steps between  
286 200 and 20eV below the edge, for 2 seconds per point in 0.4 eV steps in the XANES region

287 from 20eV below to 80 eV above the edge, and for 4 seconds per point in 0.06  $k$  unit steps  
288 in the EXAFS region from 80 to 1000eV above the edge.

### 289 **3.3 Post Run Analysis and Interpretation**

#### 290 *3.3.1 S - XANES*

291 XANES spectra for Mn, W, Ni and S were loaded into the Athena (Ravel and Newville,  
292 2005) software package, which was used for visualisation and manipulation of the data. The  
293 multiple spectra from each glass composition were checked for repeatability, averaged, and  
294 normalised to an edge step of one, where the edge step was obtained from the difference  
295 between a straight line fit to the pre-edge points and a polynomial fit to the the post-edge  
296 points extrapolated back to the absorption edge. Spectra for the sulphur standards were  
297 corrected for self-absorption using the routine embedded in Athena. The need for self-  
298 absorption corrections for the synthetic and natural glasses was assessed using the same  
299 routine and was found to be negligible. The position of the main edge was taken to be  
300 recorded by the position of the maximum first derivative for each spectra. S K edge spectra  
301 were compared with those of the sulphide and sulphate standards as a first order attempt  
302 to identify speciation via a fingerprinting approach.

303 The peak deconvolution facility embedded in Athena was used to quantify the relation-  
304 ships between XANES and sample compositions. Initial fitting attempts were used to refine  
305 the number of peaks, peak shape and peak values. Subsequent fits with set peak positions  
306 were used to solve for unknown peak areas and widths. The final fitting process utilised,  
307 for Mn and Ni bearing samples, Lorentzian peaks centred at 2473.1 eV, 2474.9 eV, 2476.2  
308 eV and, where such a peak was present, at 2481.4 eV. These peaks were superimposed on a  
309 arctan function at 2470.8 eV. W-bearing samples required an additional Lorentzian centred  
310 at 2469.8 eV, which is subsequently referred to as the W peak. The width of the arctan  
311 function was set to 0.3, and the widths and amplitudes of the other peaks were solved for  
312 simultaneously by the program. Fits were stable and converged to the same values for a

313 wide range of starting guesses. The stated uncertainties are propagated from analytical un-  
314 certainties based on the noise level of the spectra, and on the goodness of fit. Correlation  
315 coefficients were calculated for ratios between peak proportions, normalised to exclude con-  
316 tributions at 2481.4 eV (sulphate signal, see discussion below), and the Ca:additive metal  
317 molar ratio.

### 318 3.3.2 Mn, W and Ni XANES and EXAFS

319 XANES for Mn, Ni and W were compared to those of the standards. Particular attention  
320 was paid to the Ni pre-edge peak, which as been shown to provide information on Ni co-  
321 ordination (Farges et al., 2001). The pre-edge peak was isolated by a manual spline fit  
322 to the main trend of the edge, and the background removed to isolate the pre-edge peak.  
323 The centroid of the pre-edge peak was then measured by fit of a Lorentzian peak to the  
324 background subtracted XANES spectra. This process was repeated two or three times to  
325 assess the sensitivity of results to the manual fitting process. The difference between the  
326 centroid energy of the sample and of NiO ( $E_{\text{pre-edge, sample}} - E_{\text{pre-edge, NiO}}$ ) was measured and  
327 compared to the calibration of Farges et al., (2001).

328 The majority of the metal spectra were identical, so the best quality spectra for each  
329 metal were averaged, the baseline was subtracted and the signal was transformed into  $k$   
330 space, multiplied by  $k^2$  to increase the signal at high  $k$  values, and exported into Artemis  
331 (Ravel and Newville, 2005). These data were Fourier-transformed and fit to the EXAFS  
332 equation (e.g. Fulton et al., 1996). QFS (Quick First Shell) models were adopted for the  
333 EXAFS fits; these are appropriate given the probable lack of long range order or structure  
334 around the metal-bearing species in the melts. Geometries and initial coordinations for the  
335 models were taken from literature sources. Mn models were based on those of McKeown  
336 et al. (2003) with octahedrally coordinated oxygens at 2.07 Å. W models were attempted  
337 for both octahedrally and tetrahedrally coordinated  $\text{WO}_3$  and  $\text{WO}_4^{2-}$  species respectively,  
338 with oxygens at 2.00 Å in the octahedrally coordinated model (Poirier et al., 2005b) and at  
339 1.78 Å in the tetrahedrally co-ordinated model (Hazen et al., 1985). Ni was modelled on

340 the assumption of formation of octahedral melt species with nearest neighbour oxygens at  
341 2.00 Å; tetrahedral QFS models were also tried and the final results were not sensitive to  
342 the initial geometry specification.

343 The Fourier-transformed spectra were initially fit for four parameters:  $n$ , the number of  
344 nearest neighbours,  $E_0$ , the energy of the edge,  $\sigma^2$ , the mean square relative displacement,  
345 which measures the disorder present in the signal, and  $\Delta R$ , the difference between the start-  
346 ing guess and modelled distance for  $i$ -O where  $i$  represents the metal of interest. These four  
347 parameters control the shape of the Fourier-transformed signal. To a first approximation,  
348 peak size increases with  $n$ , peak position is related to  $E_0$  and  $\Delta R$ , and peak breadth increases  
349 with  $\sigma^2$ .

350 The fit value of  $n$  can represent an average co-ordination, so, for example, a value of 5  
351 could represent a mixture between tetrahedrally and octahedrally co-ordinated cations with  
352 similar bond lengths and comparable melt species geometry. Fits were tried that utilised an  
353 additional fit parameter,  $c3$ , the third cumulant, which measures the asymmetry in the signal  
354 disorder, but fits were no better, uncertainties did not decrease, and values of  $c3$  were within  
355 error of zero. For these reasons the fits documented here used a set  $c3$  of zero. Estimates  
356 for numbers of nearest neighbours require specification of  $S_0^2$ , the passive electron reduction  
357 factor, which is multiplied by the number of neighbours in the EXAFS equation (see Fulton  
358 et al. (1996) for details).  $S_0^2$  for Mn was taken to be 0.75 (after McKeown et al., 2003),  
359 and to be 1 for W and Ni. The value of 1 is probably an overestimate as  $S_0^2$  generally falls  
360 between 0.8 and 1, so numbers of nearest neighbours for W and Ni may be underestimated  
361 by up to 20%.

362 The  $k$ -range for fitting was taken to run from the first node in the  $k$  oscillations outside the  
363 XANES region i.e. at around 20-60eV, to the last node before excessive noise destroyed signal  
364 quality. This led to  $k$ -ranges for the fits from around 3 to around 9 for all Mn, W and Ni. Fits  
365 were considered successful when the R-factor for the fit was less than 0.05. The sensitivity  
366 of the fit to input parameters such as  $k$ -range and  $k$ -weighting was also explored and fits  
367 that were excessively affected by changes in these parameters were rejected. Uncertainties  
368 were taken from the Artemis output and reflect the combination of the effects of statistically

369 derived uncertainties in the signal and correlations between the fit parameters. Final fits  
370 for Ni utilised a set value for the edge energy, which was specified to be the energy at the  
371 maximum first derivative of the edge, because correlations between the fit parameters led  
372 to a relatively unconstrained solution when the edge energy was allowed to vary freely. The  
373 best fit value for the edge energy should not be significantly different to that of the centre  
374 of the edge, so this assumption is justified. Fits for Mn and W allowed  $E_0$  to vary and its  
375 proximity to the measured edge was used as a complementary measure of fit quality.

376 <end small type>

377

378

## 4 RESULTS

### 379 4.1 Characteristics of synthetic silicate glasses

380 The appearance and composition of the glasses are described in detail in Evans et al. (2008a).  
381 However, essential details are summarised briefly here. Most of the samples formed translu-  
382 cent clear or yellow-coloured glass beads up to 5mm in diameter and 0.05 to 0.15g in weight.  
383 A number of samples contained bubbles and/or black specks. In most cases the black specks  
384 occurred on the margins of the sample, or showed dendritic form in fractures but appeared  
385 to be a surface feature, probably produced on quench, and of insufficient size for analysis.  
386 However, in some Ni-bearing samples specks were distributed through the glass and appeared  
387 to define flow patterns; probe analysis (Evans et al. 2008a, not shown here) revealed that  
388 this apparently exsolved material contained Ni and S with minor Fe. XANES features of  
389 these samples are discussed below. Multiple microprobe analysis produced good repeatabil-  
390 ity in the results for over 90% of the samples analysed, which supports the proposal that  
391 equilibrium was attained in most cases. A small number of the glasses produced high to-  
392 tals, up to 102 wt%. These totals are associated with slightly higher Si contents (Table 2),  
393 and are therefore attributed to issues with Si analysis which have been noted previously on  
394 this machine. Concentrations of other elements such as Mn, W, Ni and S were checked by



395 comparison against a secondary standard, and shown to be reliable, so the implications and  
396 conclusions of this study are unaffected.

397 Runs without added Mn, W, Ni produced a dissolved S concentration for the CMAS  
398 composition of  $0.199 \pm 0.026$  wt % (19 analyses - see Evans et al., 2008 for details). Sulphur  
399 content was positively correlated with Mn concentration for the data from the Mn-bearing  
400 experiments (Table 2a); sulphur contents were lower at the same Mn content for the more  
401 oxidising experimental conditions. S content is effectively independent of W content (Table  
402 2b) and in runs where  $\log fO_2$  was increased above -9.6, the S content drops below detection  
403 limits for all samples with appreciable W (Evans et al., 2008). Such samples are not discussed  
404 here. Ni and S are negatively correlated, with an inverse relationship between S and Ni (Table  
405 2c). This is consistent with equilibration of the melt with a Ni sulphide phase, which was  
406 observed to have exsolved from the melt in many of the samples (Evans et al., 2008). Low  
407 Fe concentrations are observed in a number of samples. This is attributed to contamination  
408 during sample preparation or synthesis. The presence of such low quantities of Fe does not  
409 affect the conclusions drawn here.

## 410 **4.2 Sulphur K-edge XANES**

### 411 *4.2.1 Standards*

412 S K edge XANES for the standards show similar characteristics to those noted in the liter-  
413 ature (e.g. Li et al., 1995; Fleet, 2005). Edge energy increases with sulphur oxidation state  
414 and with degree of ionicity of bonding at any given oxidation state (Figs 1b,2). The lowest  
415 energies are found for FeS and NiS with energies of 2468.7 and 2469 eV respectively. The  
416 edge for  $WS_2$ , which also contains S as  $S^{2-}$ , occurs at slightly higher energy (2470.3 eV),  
417 and is coincident with the edge for  $FeS_2$ , which contains  $S^-$ . The edge energy for MnS is  
418 2470.7 eV, significantly higher than for FeS, which is interesting given the similar effects  
419 that  $Mn^{2+}$  and  $Fe^{2+}$  have on S solubility. The non-transition element monosulfides, CaS  
420 and MgS, have higher energies again, with edges at 2471.2 and 2471.8 eV respectively. Edge

421 energy for the sulphates occurs 10-12 eV higher than for the sulphides. The identity of the  
422 cation in a sulphate compound has much less effect on the edge energy than for sulphides  
423 (Fig. 3), with the edges for  $\text{FeSO}_4$  and  $\text{MnSO}_4$  at 2480.2, and that for  $\text{NiSO}_4$  at 2480.8 eV.  
424 The reason for this insensitivity is that O is the nearest neighbour to S in sulphates, so the  
425 cation has a much weaker effect on the local electronic environment than it does in the case  
426 of the sulphides. Note that tabulated energies (Tables 1 and 2) are edge energies rather than  
427 peak energies, which are tabulated in some literature sources (e.g. Li et al., 1995). Edge  
428 energies are used here because they are less sensitive to self absorption artifacts than peak  
429 energies.

430 The spectra for NiS, FeS and  $\text{WS}_2$  also show a small peak at around 2481eV (Fig. 2). This  
431 is in the same position as the sulphate peak, and is attributed to minor standard oxidation  
432 during sample storage that was not detected by the pre-run XRD analysis. It is unlikely  
433 to be due to oxidation during sample preparation because the MnS standard, which is very  
434 prone to oxidation, does not show such features in spite of identical preparation methods.

#### 435 4.2.2 *Synthetic silicate glasses*

436 S K edge spectra for synthetic silicate glasses without sulphide exsolution were significantly  
437 different to the spectra of any of the sulphide or sulphate standards (Fig. 4). Well resolved  
438 spectra with sufficient information for further quantitative analysis were obtained for samples  
439 with S contents greater than 0.18 wt%. Less well resolved spectra with limited information  
440 were obtained for samples with S contents between 0.02 and 0.18 wt%.

441 The main features exhibited by the silicate glass XANES were (1) a composite peak with  
442 an edge, for the majority of samples, between 2470 and 2471.5 eV (Fig. 4, Table 2). Mn-,  
443 W- and Ni-bearing glasses all produced this peak and its edge energy was not systematically  
444 related to sulphur or metal content, or to run conditions. Uncertainties in the edge position,  
445 based on measurements of the edge energy from the three spectra for each sample, are of the  
446 order of 0.3 eV. Interpretation of the composite peak is discussed further below. Ni-bearing  
447 samples from one run, B010806, exhibited edge energies slightly lower than the norm for this

448 composite peak (Table 2c) but the duplicate of this run, B140906, did not produce the lower  
449 edge energies. B010806 samples contained black specks inferred to be exsolved NiS while  
450 B140906 did not. However, S contents in the Ni-bearing samples were low, so the spectra  
451 are noisy and difficult to interpret unambiguously; (2) a low energy peak at around 2469  
452 eV that was produced only by the W-bearing samples with W contents greater than 1 wt%  
453 (runs B141106 and B220806). Run B150906, which contained W contents less than 1 wt %,  
454 produced spectra without a discernible 2469 eV peak, referred to hereafter as the W peak;  
455 (3) A peak in the same place as that for the sulphate standards with an edge at 2480.8 eV.  
456 The size of this peak relative to that of the composite peak was not related in a systematic  
457 way to sample composition, preparation methods or experimental run conditions.

#### 458 4.2.3 Spectral Deconvolution

459 Good fits (all  $\chi^2 < 2$ , Table 3, Fig. 5) were obtained for the CMAS, CMAS+Mn, and  
460 CMAS+W glasses with sulphur contents greater than 0.18 wt%. It was not possible to  
461 obtain unique solutions to the fits for the Ni-bearing glasses because the sulphur contents  
462 were low and the signal:noise ratio was too low to uniquely constrain the size of the four  
463 peaks. The proportional area of each of the peaks were calculated (Table 3). Two samples  
464 with proportional areas for the sulphate peak at 2481.4 eV greater than 20% (B310706p5 and  
465 B151106p1) were excluded from further analysis (see discussion) because post-run oxidation  
466 is sufficient to have seriously affected the distribution of sulphur species in the sample.

467 Results (Table 3, Table 4, Fig. 6) showed that there was a good correlation between  
468 the proportional areas of the 2473.1 eV peak and the molar Ca:Mn ratio ( $r=-0.84$ , Fig. 6a)  
469 and between the 2474.9 eV peak and the molar Ca:Mn ratio ( $r=-0.84$ , Fig. 6b). These  
470 values are significant at the 95% level. Significant correlations were also noted between the  
471 Mn concentration and the proportional areas of peaks at 2473.1 eV and 2476.2 eV, and the  
472 sulphur concentration and the proportional areas of peaks at 2473.1 eV and 2476.2 eV (Table  
473 4). Mn-bearing glasses from two different runs lie on the same trend. No such correlation  
474 was noted between peak proportions and the Ca:W ratio or other compositional parameters

475 in the W-bearing samples (Fig. 6c, d). The correlation coefficient for the 2473.1 eV peak  
476 and the molar Ca:W ratio was -0.43, while that for the 2474.9 eV peak and the molar Ca:W  
477 ratio was 0.06. These values are not consistent with a statistically significant correlation.  
478 The area of the W peak did not relate systematically to W content, but the peak was poorly  
479 resolved so systematic relationships may not have been detectable by this method.

### 480 4.3 Mn, W and Ni K-edge XANES and EXAFS

#### 481 4.3.1 Standards

482 Standard spectra are consistent with those described in the literature (e.g. McKeown et al.  
483 (2003); O'Neill et al., (2008)). MnO (Fig. 7a) shows a pronounced white line and a small  
484 pre-edge peak, while MnO<sub>2</sub> shows a larger pre-edge peak but a much less intense white line.  
485 The spectra for MnS has a lower edge energy, and lacks any pre-edge peak. W spectra are  
486 sensitive to the oxidation state of W, with a lower edge energy for tetravalent W in WS<sub>2</sub>,  
487 and higher values for hexavalent W in WO<sub>3</sub> and CaWO<sub>4</sub>. Tetrahedrally co-ordinated W  
488 in CaWO<sub>4</sub> shows a post-edge bump (Fig. 7b), which is absent in the spectra derived from  
489 octahedrally co-ordinated W in WO<sub>3</sub>. Ni spectra also show increasing edge energy with  
490 increasing oxidation state (Fig. 7c). NiO and NiS spectra are distinctly different, with a  
491 pronounced pre-edge peak present in the NiO spectra.

#### 492 4.3.2 Synthetic silicate glasses

493 Mn XANES spectra from the glasses resemble that of MnO (Figs 7a and 8a), and the edge  
494 position closely matches that of MnO standards measured by McKeown et al. (2003). This  
495 implies that Mn is present as the divalent state in the silicate glass. There is no discernible  
496 variation in the XANES spectra as a function of Mn:S ratio in the melt (Fig. 8a) or the  
497  $\log f_{\text{O}_2}/f_{\text{S}_2}$  of experiment. The Fourier transform of the EXAFS signal shows a single peak.  
498 The shape, location and size of this peak provides information on the nearest neighbours

499 to Mn in the silicate glass. EXAFS fitting (Fig. 9a) is consistent with Mn surrounded by  
500  $5 \pm 1$  oxygen neighbours at a distance of  $2.06 \pm 0.02 \text{ \AA}$  (Table 5). Acceptable fits are not  
501 produced for other attempted models. The bond-length is a useful indicator of coordination;  
502 McKeown et al. (2003) show that tetrahedral divalent Mn in crystalline silicates and oxides  
503 has a Mn-O distance close to  $2 \text{ \AA}$ , 5 co-ordinated divalent Mn has a Mn-O distance close  
504 to  $2.15 \text{ \AA}$ , and octahedral divalent Mn has a Mn-O distance closer to  $2.2 \text{ \AA}$ . It is therefore  
505 likely that Mn co-ordination is at the lower end of the fit range.

506 L3 edge XANES spectra for the W-bearing glasses (Fig. 8b) are all very similar to those  
507 of O'Neill et al. (2008), who demonstrated from solubility measurements that W dissolves  
508 in silicate melts in the 6+ oxidation state at the conditions relevant to this study. The  
509 spectra exhibit an intense white line (A) and a post-edge bump (B) before the EXAFS  
510 oscillations begin. The post-edge bump is similar but less intense than that shown by  
511 tetrahedrally co-ordinated W in  $\text{Na}_2\text{WO}_4$  (Fig. 7b) and scheelite,  $\text{CaWO}_4$  (Farges et al.,  
512 2006). There is no systematic change in spectra as a function of the oxidation state of the  
513 experiment, W:S ratios or absolute W and S contents. Linear combination fitting of the  
514 spectra to the two standards using the facility in Athena indicates that a contribution from  
515 the tetrahedrally coordinated component alone reproduces the spectra best; addition of an  
516 octahedrally coordinated component does not improve the fit. There is no evidence for a  
517  $\text{WS}_2$  component. The EXAFS for the W-bearing samples fit well to a model based on a  
518 tetrahedral arrangement of four oxygens at  $1.75 \text{ \AA}$  from a central W atom (Table 5, Fig.  
519 9b). EXAFS analysis in which the W-bearing spectra were fit to a  $\text{WO}_3$  model, with six  
520 oxygens at an average of  $2.00 \text{ \AA}$  distance were unsuccessful. Further attempts in which the  
521 oxygens were allowed to vary in distance as described by Poirier et al. (2005b) did not  
522 improve the fit quality. These results confirm the suggestion of O'Neill et al. (2008) that  
523 W occurs in the 6+ state in silicate melts, and are consistent with the presence of W in the  
524 silicate melts investigated here as  $\text{WO}_4$  tetrahedra.

525 Ni K edge XANES spectra for the Ni-bearing glasses are qualitatively similar to those  
526 reported by Farges et al. (2001) for divalent Ni in [4], [5] and [6] coordination and superficially  
527 resembles that of the NiO standard (Fig. 7c, 8c). The structure is slightly simpler than that

528 for NiO, however; post-edge complexities are absent in the glass spectra, which is consistent  
529 with a resonance cause for the features; a lack of long range structure in the melts will  
530 dampen the resonances. There is no systematic change in spectral shape as the Ni:S ratio  
531 changes from much greater than 1 in sample B190906p5 to much less than 1, e.g. in sample  
532 B231205p5 (Fig. 8c). Nor do the spectra depend on the oxygen and sulphur fugacities at  
533 which the glasses formed (not shown).

534 The difference between centres of the pre-edge peak and that of the NiO standard are 0.4  
535 to 0.6 eV (Table 6). This is consistent with [4] coordinated Ni in the silicate glass according  
536 to the calibration of Farges et al. (2001). However, absolute energies of the pre-edge peaks  
537 are slightly but systematically different to those recorded by Farges et al. (2001). The pre-  
538 edge peaks from this study are centred at 8332.5 to 8332.7 eV, relative to the pre-edge peak  
539 of NiO, which is fit by a Lorentzian centred at 8333.15 eV. The results described by Farges et  
540 al. (2001) for [4] coordinated glasses are based on peaks centered around energies of around  
541 8330.8 eV relative to NiO at 8331.25 eV. The source of the discrepancy is unclear, as both  
542 studies are based on calibration of the Ni metal edge at 8333 eV, and non-linear calibration  
543 effects would not be expected to be significant so close to the calibration point.

544 Fits to the EXAFS yield  $3.8 \pm 0.9$  nearest neighbour oxygens at  $1.96 \pm 0.01 \text{ \AA}$  (Table 5,  
545 Fig. 9c), which is consistent with the coordination inferred from the pre-edge peak. Other  
546 fit parameters (Table 5) are also consistent with results reported by Farges et al. (2001).  
547 The possibility that Ni in 4 coordination has oxygens at two distinct Ni-O distances was also  
548 investigated but the data was insufficient to distinguish between this model and the single  
549 Ni-O distance model, so the simpler model was preferred.

### 5.1 Origin of peak at 2481 eV in nominally $S^{2-}$ -bearing glasses

The similarity of the position of the peak at 2481 eV to the main peak in the sulphate standards is consistent with a  $S^{6+}$  source for the 2481 eV peak. The peak is therefore referred to subsequently as the sulphate peak. The proportion of the signal associated with this peak, which was obtained from the spectra deconvolution described above, ranged from zero, i.e. the peak was not detectable, to 68% (Table 3). The proportion of the sulphate peak was greater than 5% for six out of the 21 samples for which robust spectral deconvolution was possible (Table 3). The proportion of the sulphate peak was not systematically related to sample sulphur content (Fig. 10a) or the duration of sample storage (Fig. 10b), although the sample with the highest sulphur content, which also had the longest storage time (112 days), had the highest proportion of sulphate peak. The presence of the sulphate peak is a concern, because the experiments were performed in the sulphide stability field so primary sulphate is not expected. However there are a number of unintended causes for the peak that should be considered.

Incorrect gas mixes or inadequate gas flows during the experiment could have resulted in samples more oxidised than intended. However this is an unlikely cause as such factors would have affected all six samples in a run, rather than just one or two, as is the case observed. For example, in run B310706, sulphate peak proportions ranged from 2% to 68%. Additionally, if sulphate were the stable redox state in the melt then sulphur solubilities would have been far smaller than those measured.

Oxidation during quench is another possibility. It has been shown that  $S^{6+}$  can be produced by cooling of natural Fe-bearing  $S^{2-}$ -bearing glasses via exchange with the  $Fe^{2+}$ - $Fe^{3+}$  redox couple (Metrich et al., 2009). However, all the runs were quenched identically, but only some samples from some runs show oxidation, as discussed for run B310706 above. Additionally, Mn and Ni are unlikely to reduce to a valence less than +2 in order to produce sulphate. W could reduce to a lower valence but the proportion of the sulphate peak in

577 the W-bearing samples is as low or lower than in the Mn and Ni-bearing samples, so this is  
578 unlikely to be a major factor.

579 Oxidation could have occurred during sample storage. The silicate glasses are highly  
580 stressed due to their rapid quenching, and are metastable under room pressure and temper-  
581 ature, and often crumbled to produce a large surface area that would have facilitated reaction  
582 subsequent to sample production. The samples were not stored with a dessicant, and the  
583 presence of water vapour would have further catalysed sample degradation and sulphate pro-  
584 duction. This proposal is supported by the higher, though variable, extent of oxidation in  
585 samples from run B310706, which was stored for the longest time prior to sample preparation  
586 and synchrotron analysis (Fig. 10a).

587 Sample preparation is known to induce oxidation (e.g. Fleet, 2005) under some circum-  
588 stances. It is for this reason that four samples were prepared in two ways, with one half of  
589 the sample prepared in acetone in air as normal, and the other half prepared in a glovebox  
590 filled with nitrogen. There was no systematic increase in the sulphate peak as a result of the  
591 preparation protocol. In two cases the nitrogen-prepared portion exhibited a higher sulphate  
592 peak (e.g. Fig. 10c), in one the portion prepared under air exhibited the higher sulphate  
593 signal (Fig. 10d), and in the final case the two signals were effectively identical (Fig. 4c).  
594 It is therefore unlikely that the sample preparation caused the oxidation. These results in-  
595 dicate that oxidised portions of the samples are heterogeneously distributed. A further test  
596 of sample preparation was made by preparation of one half of a sample with acetone under  
597 air, and the other dry, but again under air. The spectra from these two splits of the same  
598 sample were effectively identical. Additionally, preparation of fresh MnS, which is highly  
599 susceptible to oxidation, by grinding under acetone did not produce S-XANES spectra with  
600 a sulphate peak (Fig. 2). Contamination introduced during sample preparation is also pos-  
601 sible. However, this cause is unlikely because the blanks of kapton tape showed no sulphur  
602 signal at all, and preparation blanks for Cl-XANES loaded with the same sample protocols  
603 (Evans et al., 2008b) showed no cross contamination between samples.

604 Beam-induced oxidation to produce tetravalent sulphur has also been observed (Wilkes et  
605 al., 2008; Metrich et al., 2009) for intense microbeams such as that employed at the ESRF.



606 The beam at the NSRRC is much less powerful, consecutive scans on the same sample do not  
607 show any increase in the size of the sulphate peak relative to the composite peak, and there  
608 is no peak for tetravalent sulphur. It therefore seems unlikely that the  $S^{6+}$  was produced by  
609 beam-sample interactions.

610 To summarise, the sporadic nature of the oxidation and the lack of systematic oxidation  
611 in any particular run argue against experimental or quench-induced oxidation. Comparison  
612 of multiple preparation techniques, repeat analyses, and preparation blanks largely eliminate  
613 the possibility that oxidation was caused during sample preparation and analysis. The most  
614 likely cause of the oxidation is reaction of the glasses during sample storage. Such oxidation  
615 does, in extreme cases, affect the shape of the composite peak (e.g. Fig. 10c,d). For this  
616 reason, samples with a sulphate peak proportion greater than 20% were excluded from further  
617 analysis. A possible concern is that sulphur oxidation could affect the metal EXAFS results.  
618 This is unlikely because metal:S ratios are sufficiently high that even complete oxidation of  
619 the sulphur would not significantly change the proportion of metal bonded to the dominant  
620 oxygen ligand.

## 621 **5.2 Evidence for tetravalent sulphur**

622 Sulphur XANES spectra are consistent with the presence of  $S^{2-}$  and  $S^{6+}$ . There is no evidence  
623 for  $S^{4+}$  in the form of an absorption peak between sulphide and sulphate, as proposed by  
624 Metrich et al. (2002). This is as expected; Wilke et al. (2008) and Metrich et al., (2009),  
625 recently showed that  $S^{4+}$  can be produced by the intense photon flux experienced by samples  
626 under a synchrotron microbeam. The experiments performed for this study used a mm-size  
627 beam and lower photon fluxes than those of Metrich et al. (2002) so beam-induced changes  
628 in sample oxidation state were avoided.

### 629 5.3 Glass composition effects on the composite peak

630 The correlations between the proportions of the different components of the composite sul-  
631 phur peak and the Ca:Mn ratio (Fig. 6a, b) provide evidence that the components of the  
632 composite peak relate to melt composition in a systematic way. The simplest interpretation  
633 would be that the lowest energy peak (2473.1 eV) is caused by Mn-S interactions in the  
634 melt, while the higher energy peaks (2474.9 eV and 2476.2 eV) are related to Mg-S and  
635 Ca-S interactions, and the W-peak at 2469.8 eV records W-S interactions.

636 Such an interpretation would, however, be over simplistic, because (a) the 2473.1 eV peak  
637 is not zero in Mn-free samples and (b) the sulphide standard spectra display composite peaks  
638 much broader than any of the component peaks found by the deconvolution process, so over-  
639 lap would be expected to occur between, for example, the Mn:S and Ca:S peak contributions.  
640 Peaks in the glass are unlikely to be narrower than those in the sulphides because glasses are  
641 much less ordered than crystalline materials, with a consequently broadened XANES signal.  
642 It is therefore likely that the deconvolution process is unable to resolve the true complexity  
643 of the XANES, and that the four or five peaks that it is possible to resolve, while useful,  
644 cannot be assigned on a 1:1 basis to any particular interaction.

645 A more reasonable proposal is that parts of the signal accounted for by the 2473.1 eV and  
646 2469.8 eV peaks can be attributed to Mn-S and W-S interactions respectively, while parts  
647 of the signal accounted for by the 2474.9 eV and 2476.2 eV peaks are caused by Ca-S and  
648 Mg-S interactions. Similar results, on qualitative level, were found by Metrich et al. (2009),  
649 for CMAS+FeO glass compositions. However, Metrich et al. (2009) only studied Fe-bearing  
650 melts with FeO greater than 10 wt%, and so were unable to correlate peak area with metal  
651 contents as shown in Fig. 6.

652 The observations can be explained in terms of the electronic configuration of alkali earth  
653 and transition metal sulphides. Transitions to the lowest unoccupied states occur at lower  
654 energies for sulphides of the more covalently bonded materials (Mn, W) and at higher energies  
655 for sulphides of the more ionically bonded materials (Mg, Ca). For Mn, the transition is  
656 likely to be to hybridised S 2p and metal unoccupied 3d orbitals (Farrell et al., 2002), while

657 for Ca and Mg, the low lying d orbitals are less available for hybridisation which causes  
658 the edge energy to increase. The energy of the peak-related transition for a hypothetical  
659 W- and S-bearing melt species is harder to determine because the valency of the W is not  
660 known and the electronic structure of the conduction band is less well studied. However,  
661 the position of a signal from W-S interactions at a lower energy than a signal from Mn-S  
662 interactions is consistent with the relative positions of the main edge in the WS<sub>2</sub> and MnS  
663 spectra, although the magnitude of the difference is larger for the glass spectra.

664 Electronic configuration is also related to the conduction properties of the equivalent  
665 crystalline sulphides. The more covalent compounds such as MnS and FeS have a smaller  
666 band-gap than the compounds with a greater ionic character such as MgS and CaS, and  
667 it is the band gap that is reflected by the slightly higher energy of the transition for the  
668 alkali earths. However, the peak energies for the glass samples are different to those for the  
669 equivalent component sulphides. This is an expected consequence of the different orbital-  
670 orbital interactions that occur in a silicate melt where the structure is more relaxed. Less  
671 complicated spectra may record the lower signal:noise ratio attainable for the lower S con-  
672 centrations in the glasses, but may also relate to a lack of mid- to long-range ordering and  
673 consequent resonances in the glass structure.

#### 674 **5.4 Features specific to the W-bearing glasses**

675 The low energy peak centred at 2469.8 eV in the S XANES spectra for the CMAS+W melts  
676 (e.g. Fig. 4a) is difficult to attribute to a particular transition because the research published  
677 on XAS and the electronic configuration of W-S compounds (Dartigeas et al., 1996; Prouzet  
678 et al., 2003) is limited and does not address this issue directly. However, the transitions  
679 that are most likely to be available to S 1s core electrons in W-S melt species are 3p S  $\sigma^*$   
680 orbitals hybridised with unoccupied levels in the W 5d orbitals. These orbitals are sparsely  
681 occupied in hexavalent tungsten so it is probable that a transition to these orbitals might be  
682 energetically favourable compared to the transitions discussed above for CaS and MgS melt  
683 species. Regardless of the precise cause of the peak, its existence suggests that S and W do

684 interact in glasses, contrary to conclusions that would be drawn from studies of S solubility  
685 in melts, which indicate that S concentrations in silicate melts are insensitive to W content  
686 (Evans et al., 2008). However, the observation cannot be taken as unequivocal evidence for  
687 W-S melt species because it is possible that the glass may not faithfully preserve all melt  
688 features.

689 Additional support for the notion that W may form W-S species in melts is provided by  
690 consideration of the nature of W bonding in melts. Tungstate species are characterised by  
691 a high average bond-valence; four co-ordinated hexavalent tungsten has a bond-valence of  
692 1.5. This means that tungsten is much more likely to attach to network modifiers, because  
693 network modifiers, which have lower charge than the network formers Al and Si, can charge  
694 balance the high valence W more easily. This observation explains why hexavalent tungsten  
695 generally occurs in non-silicate minerals in nature, and the strong dependence of hexavalent  
696 tungsten solubility on Ca concentration in melts (O'Neill et al., 2008). It may also indicate  
697 that W forms species that combine network modifying cations *and* sulphur. However further  
698 work would be required to investigate this possibility.

## 699 **5.5 Linear combinations of sulphide spectra**

700 Theoretical spectra for mixtures of the standards were calculated to explore the similarity of  
701 spectra to those for mixtures of the component sulphides. Mixed spectra were calculated as  
702 a molar proportion-weighted sum of the spectra for the individual standards (Fig. 11). Rela-  
703 tive weights were taken from expressions for S solubility as a function of metal concentration  
704 by O'Neill and Mavrogenes (2002) and Evans et al. (2008a). Validity of the comparison  
705 relies on the assumption that the intensity of the S K- $\alpha$  signal is proportional to the S  
706 concentration and is not affected by the individual environment of the S. This assumption  
707 has been shown to be valid over a range of sulphur contents for metal sulfide solid-solutions  
708 (Farrell and Fleet, 2000; 2001; Farrell et al., 2002) and low concentrations of sulphur in coals  
709 (Huffman et al., 1991).

710 XANES spectra of the silicate glasses are not similar to those constructed by linear

711 combination of spectra from the component sulphides (Fig. 11). This is in contrast to the  
712 results of Fleet (2005), who found that XANES of S in synthetic and natural glasses could be  
713 produced by a simple combination of the sulphides of the cations present in the samples. The  
714 discrepancy might be attributable to (a) lower signal:noise of the Fleet samples, which had  
715 lower sulphur contents than those for which results are presented here; or (b) the combination  
716 of digitised spectra for CaS and MgS standards from one beamline with measured spectra  
717 from another. The CSRF has a resolution of about 0.9 eV at the S K edge (Farrell et al.,  
718 2002) and resolution at the NSRRC is around 0.5 eV. Thus features may appear sharper in  
719 data from the NSRRC, as shown by a comparison between data for FeS in this work and in  
720 Fleet (2005) (not shown). However, there may be other factors that influence the differences  
721 between the spectra. Such factors have not been brought to light by the results of this study,  
722 and remain mysterious.

## 723 **5.6 Evidence for formation of metal-S melt species from metal XAS**

724 Mn XANES spectra are very similar to those of Mn-bearing borosilicate waste glasses (McK-  
725 eown et al., 2003), for which divalent Mn co-ordinated with O was inferred. Mn spectra show  
726 no evidence of changes to Mn speciation with increases in S:Mn ratio, and the spectra are  
727 consistent with O as the nearest neighbour to divalent Mn. Influences of S in the first coordi-  
728 nation shell would be expected to manifest in the form of a reduction in the edge energy and  
729 loss of the pre-peak feature at 6540.5 eV. Similarly, spectra from CMAS+Ni and CMAS+W  
730 glasses show no evidence for a change in spectral features with changing sulphur content. It  
731 should be possible to detect the presence of significant quantities of a Ni-S species because  
732 the NiS spectra lacks the pre-edge peak shown by NiO and has a lower edge energy. Ex-  
733 pected changes for W would be much less because the W L3 edge is less sensitive to changes  
734 in local environment than the K edges for Mn and Ni.

735 The lack of evidence for formation of metal-S melt species from the metal XAS is, at  
736 first sight, contradictory with evidence from the S XAS that supports metal-S interactions.  
737 However, the apparent contradiction can be reconciled if the potential proportions of metal-S

738 and metal-O species are considered. The maximum proportion of the additive metals Mn,  
739 W and Ni that could form melt species with sulphur,  $p_{\max}$ , was calculated from

$$740 \quad p_{\max} = \frac{n_S - n_{S,\text{CMAS}}}{n_{\text{metal}}} \quad (1)$$

741 where  $n_i$  is the number of moles of melt component  $i$  per unit mass.  $n_{S,\text{CMAS}}$  is the number of  
742 moles of S in the end-member CMAS composition. Values could only be calculated reliably  
743 for the experiments performed at a  $\log_{10} f\text{O}_2$  of -9.6 and  $\log_{10} f\text{S}_2$  of -1.91 as these were the  
744 conditions at which the S content of the CMAS composition was best constrained. Values  
745 for the Mn-bearing glasses were between 10 and 20%, those for the W-bearing glasses were  
746 lower at 1 to 2 %, and those for the Ni-bearing glasses were meaningless, because the loss of  
747 the immiscible sulphide phase led to a drop in S content to below the CMAS value.

748 The absolute maximum ratio of metal:S to metal:O species is therefore 0.2. At this level,  
749 the relatively subtle effects on the metal XAS caused by the presence of metal:S species  
750 would be difficult to distinguish, as changes in the size of the pre-edge feature of up to 20%  
751 are within the uncertainties of the measurement technique. Thus, the metal XAS provides  
752 information on the dominant metal complexing agent, which is oxygen, but lesser quantities  
753 of metal-S melt species are not precluded.

## 754 **5.7 Glass composition effects on metal-O coordination**

755 Previous work has inferred that W coordination in silicate melts can be octahedral (Poirier  
756 et al., 2005a,b; Farges et al., 2006) or tetrahedral (Farges et al., 2006; O'Neill et al., 2008).  
757 EXAFS and XANES results from this work are consistent with dominantly tetrahedrally  
758 coordinated W. Work that found octahedral coordination used Si and Al-free melts (Poirier et  
759 al., 2005b), whereas the lower coordinations were found for Si- and Al-bearing glasses (Farges  
760 et al., 2006). A similar phenomena is noted for the CMAS+Ni melts. Ca-dominated melts  
761 are shown by Farges et al. (2001) to contain Ni in [5] or greater coordination whereas this  
762 study found pre-edge peaks and EXAFS analysis to indicate somewhat lower coordination  
763 of [4] to [5]. A significant difference between the melts in the two studies is the higher Si

764 and Al content in the CMAS composition, with a significant reduction in the proportion of  
765 oxygen that is non-bridging.

766 A possible explanation for these observations is that a reduction in the availability of  
767 non-bridging oxygens, which occurs when a significant proportion of oxygen is involved in  
768 the polymeric Si-Al framework of the melt, produces a lower coordination for W and Ni.

## 769 6 CONCLUSIONS

770 Sulphur spectra for CMAS, CMAS+MnO, CMAS+NiO and CMAS+WO<sub>3</sub> are broadly sim-  
771 ilar, consisting of a broad composite peak plus a variable sulphate signal that is attributed  
772 to sulphur oxidation during sample storage. CMAS+W exhibits an additional peak at lower  
773 energy that is tentatively attributed to transition between S 1s electrons into a hybridised  
774 W 5d - S 3p  $\sigma^*$ -anti-bonding orbital. There is no evidence for quadravalent sulphur at the  
775 low pressures and relatively reduced conditions explored here.

776 Decomposition of the S K-edge XANES into four component Lorentzian peaks plus an  
777 edge step reveals a systematic relationship between peak area and sample composition for  
778 the CMAS+Mn melts. Mn:Ca ratios are correlated positively with the proportion of the  
779 lower energy peak (2473.1 eV) and negatively with the proportion of the peak at 2474.9  
780 eV. The correlations are significant at the 95% level. Such changes were not noted for the  
781 CMAS+W and CMAS+Ni spectra. However, low sulphur contents in CMAS+Ni glasses  
782 resulted in low resolution spectra which hinder recognition of changes such as those noted  
783 for CMAS+Mn.

784 Changes in the composite peak shape are consistent with known characteristics of metal-  
785 S bonding. Metals that show a greater covalent character in bonding with S, such as Mn,  
786 have lower energy hybridised orbitals available, and transitions into these orbitals produce a  
787 contribution to the lower energy peak component at 2473.1 eV. Metals that show metal-S  
788 bonds with a more ionic character, such as Mg and Ca, have higher energies for the S K-  
789 edge because the hybridised orbitals are less available. Thus a large proportion of the signal

790 accounted for by the 2474.9 eV and 2476.2 eV peaks in the composite peak is attributed to  
791 transition of 1s S electrons into S-Ca or S-Mg hybridised orbitals. A 1:1 association between  
792 the deconvoluted peaks and the transitions is unlikely because the true complexity of the  
793 spectra is likely to have been beyond the resolving power of the deconvolution exercise.  
794 Nevertheless, the results provide good evidence for formation of Mn-S and W-S melt species  
795 in silicate glasses.

796 Measured spectra were demonstrated not to be any plausible combination of the com-  
797 ponent sulphide spectra. The difference between the component sulphide and glass spectra  
798 demonstrates that the electronic configuration of S-bearing species in the glasses is quantita-  
799 tively different to that in the sulphides, although the same processes and elemental properties  
800 can be used to provide a qualitative explanation of the observed phenomena.

801 XANES and EXAFS analysis of Ni, W and Mn can be explained by formation of metal-O  
802 melt species and there is no evidence for metal-S bonding, although such evidence would  
803 be hard to distinguish, given the low S:O ratio and calculated maximum contributions of  
804 metal-S species to the spectra. Mn is likely to be divalent and be coordinated by 4 to 5  
805 oxygens at a distance of 2.06 Å, consistent with the results of previous work. W is likely  
806 to be tetrahedrally coordinated with oxygens at a distance of around 1.75 Å, in groups  
807 similar to those found in scheelite. Ni EXAFS and pre-edge peak properties are consistent  
808 with 4 coordinated Ni-O melt species with Ni-O distances of 1.96 Å. Ni and W both show  
809 coordinations lower than those found for previous works that utilised melt compositions with  
810 a lower proportion of bridging oxygens. This observation leads to the proposal that metal:O  
811 coordination is a function of the ratio of bridging to non-bridging oxygens.



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# TABLES



Table 1: Summary of run conditions

Run	Additive metal	Additive conc (wt%)	$\text{Log}_{10} f\text{O}_2$	$\text{Log}_{10} f\text{S}_2$	$\text{Log}_{10} f\text{SO}_2$	$\Delta\text{QFM}$
B030106	Mn	1-10	-9.60	-1.91	-3.06	-3.2
B310706	Mn	1-10	-9.60	-1.91	-3.06	-3.2
B020806	Mn	1-10	-7.18	-0.84	-0.61	-0.7
B111006	Mn	0-1	-7.59	-2.80	-1.50	-1.2
B151106	Mn	0-1	-9.60	-1.91	-3.06	-3.2
B301205	W	0-1	-9.60	-1.91	-3.06	-3.2
B240306	W	1-10	-9.60	-1.91	-3.06	-3.2
B220806	W	1-10	-9.60	-1.91	-3.06	-3.2
B230806	W	1-10	-7.18	-1.85	-0.61	-0.7
B150906	W	0-1	-9.60	-1.91	-3.06	-3.2
B200906	W	1.5-10	-3.09	-10.85	-0.52	3.3
B141106	W	1-10	-9.60	-1.91	-3.06	-3.2
B231205	Ni	0-1	-9.60	-1.91	-3.06	-3.2
B220306	Ni	1-10	-9.60	-1.91	-3.06	-3.2
B070406	Ni	10-30	-9.60	-1.91	-3.06	-3.2
B120406	Ni	1-10	-7.18	-1.85	-0.61	-0.7
B010806	Ni	0-1	-9.60	-1.91	-3.06	-3.2
B030806	Ni	0-1	-7.18	-1.85	-0.61	-0.7
B140906	Ni	0-1	-9.60	-1.91	-3.06	-3.2
B190906	Ni	1-10	-3.09	-11.88	-1.52	3.3

960

Table 2a: Electron microprobe analyses of Mn-bearing samples

Sample	Si(wt%)	Al(wt%)	Mg(wt%)	Ca(wt %)	Fe(wt%)	S(wt%)	Mn(wt%)	O(wt%)	Total(wt%)	Edge (eV)
B030106p2 ‡	19.93(8)	6.64(4)	5.07(3)	24.54(5)	0.73(1)	0.224(1)	0.381(3)	42.31(1)	99.9(2)	n.a.
B310706p1 *	20.3(1)	6.98(6)	5.43(5)	25.32(9)	0.018(1)	0.196(3)	bdl	43.2(2)	101.5(5)	2471.3
B310706p2 *	19.5(1)	6.91(2)	5.35(7)	24.91(1)	0.04(2)	0.332(3)	2.07(2)	42.8(1)	102.0(2)	2470.4
B310706p3 *	18.9(2)	6.58(9)	5.17(7)	24.2(2)	0.043(9)	0.480(2)	3.74(5)	42.0(4)	101.1(8)	2470.5
B310706p4 *	18.4(1)	6.44(2)	5.06(2)	23.71(7)	0.05(1)	0.726(6)	6.03(2)	42.0(1)	102.4(2)	2470.4
B310706p5	18.2(1)	6.3(1)	4.87(7)	23.24(7)	0.07(3)	0.879(4)	7.15(2)	41.8(1)	102.5(3)	2470.6
B310706p6 *	17.6(2)	6.10(9)	4.76(7)	22.36(6)	0.06(2)	1.117(8)	8.74(3)	41.2(2)	102.0(4)	2470.9
B020806p1	17.6(2)	6.19(3)	4.75(1)	22.62(5)	bdl	0.088(3)	9.008(1)	40.5(2)	100.8(4)	2470.8
B020806p2 *	18.40(5)	6.39(2)	4.993(3)	23.76(8)	0.02(2)	0.053(2)	6.10(3)	41.25(9)	101.0(2)	2471.4
B020806p3 *	17.93(5)	6.3(1)	4.92(8)	23.29(3)	0.040(7)	0.12(1)	7.27(2)	40.8(2)	100.7(3)	2470.5
B020806p4	19.4(1)	6.76(5)	5.29(9)	25.07(8)	bdl	0.024(2)	2.122(7)	42.3(2)	101.0(3)	2470.5
B020806p5	19.12(5)	6.69(4)	5.09(8)	24.62(6)	bdl	0.039(2)	3.902(7)	42.10(5)	101.6(1)	2471
B020806p6 ‡	18.1(1)	6.3(1)	4.87(7)	23.3(1)	bdl	0.122(4)	7.24(2)	41.0(2)	101.0(4)	2471.2
B111006p2	20.2(5)	7.6(7)	4.9(8)	24.(1)	bdl	0.019(7)	1.02(9)	43.0(3)	101.2(2)	n.a.
B151106p1	21.08(9)	7.08(4)	5.25(2)	22.03(7)	0.048(7)	0.229(2)	0.379(5)	42.93(9)	99.1(1)	2471.2
B151106p4	20.84(5)	6.95(6)	5.20(2)	21.93(6)	0.05(2)	0.274(5)	1.070(6)	42.7(1)	99.2(2)	2471.4
B151106p5	21.19(4)	7.02(7)	5.22(6)	22.02(6)	0.096(8)	0.219(7)	0.235(3)	42.94(4)	99.0(1)	2471.2
B151106p6	20.89(7)	6.95(3)	5.18(6)	21.82(6)	0.065(4)	0.251(4)	0.840(7)	42.62(9)	98.7(1)	2471.5

\*: S XANES depicted

‡: Mn XANES depicted

n.a.: not available

Table 2b: Electron microprobe analyses of W-bearing samples

Sample	Si(wt%)	Al(wt%)	Mg(wt%)	Ca(wt %)	Fe(wt%)	S(wt%)	W(wt%)	O(wt%)	Total(wt%)	Edge (eV)
B301205p3 ‡	19.8(1)	6.65(6)	5.15(5)	24.38(2)	0.486(7)	0.208(2)	0.740(6)	42.1(2)	99.6(3)	n.a.
B240306p1	20.60(6)	7.32(6)	5.55(1)	15.53(3)	0.06(1)	0.075(4)	7.74(4)	41.97(9)	98.9(2)	n.a.
B220806p2	21.59(1)	7.63(9)	5.80(5)	16.03(5)	0.048(1)	0.064(4)	5.86(4)	43.23(1)	100.3(2)	2469
B220806p3	21.1(1)	7.39(7)	5.69(5)	15.50(7)	0.05(1)	0.068(7)	7.6(1)	42.6(1)	100.0(3)	2468.8
B220806p4	23.08(5)	8.14(5)	6.14(7)	16.77(2)	0.020(7)	bdl	2.23(3)	44.92(9)	101.4(2)	n.a.
B220806p5	22.8(2)	7.89(3)	6.09(6)	19.73(2)	0.06(2)	0.073(5)	0.223(7)	45.0(2)	101.9(4)	2469
B220806p6	20.51(9)	7.32(7)	5.6(1)	15.1(2)	0.05(1)	0.071(3)	9.27(5)	42.1(2)	100.1(6)	2470.6
B230806p5 ‡	22.8(2)	8.00(8)	6.2(1)	16.6(1)	bdl	bdl	2.34(4)	44.4(4)	100.3(9)	n.a.
B200906p5 ‡	19.2(1)	6.61(8)	5.31(7)	24.46(4)	bdl	bdl	2.67(4)	41.7(1)	100.0(3)	n.a.
B150906p1	19.7(2)	7.0(3)	5.5(5)	25.1(3)	bdl	0.3(1)	0.70(9)	42.9(2)	101.4(4)	2471.1
B150906p2	20.1(1)	6.93(6)	5.36(6)	25.1(1)	0.040(5)	0.200(3)	0.28(3)	42.9(2)	101.0(4)	2471.2
B150906p3	19.7(1)	6.83(5)	5.39(9)	24.95(7)	0.18(2)	0.206(4)	0.89(3)	42.5(2)	100.7(3)	2471.4
B150906p4	19.9(1)	6.89(6)	5.4(1)	25.14(9)	0.17(2)	0.202(5)	0.49(5)	42.7(2)	101.0(3)	2471.2
B150906p5	21.16(3)	7.32(1)	5.80(8)	22.80(9)	0.163(7)	0.134(2)	bdl	43.7(1)	101.1(3)	2471.4
B141106p1 *	18.4(3)	6.6(2)	5.16(5)	22.0(3)	0.07(2)	0.14(2)	6.4(2)	40.9(7)	100.(2)	2468.9
B141106p2 *	19.5(2)	6.8(4)	5.2(3)	24.8(8)	bdl	0.10(2)	2.4(2)	42.1(6)	101.(1)	2469.0
B141106p3	20.2(7)	6.7(4)	5.1(8)	23.5(8)	0.01(2)	0.05(4)	3.8(1)	42.7(6)	102.(2)	2469.5
B141106p4	17.57(8)	6.22(4)	5.27(5)	20.55(9)	0.05(3)	0.18(5)	10.1(4)	40.1(2)	100.0(6)	2470.6

\*: S XANES depicted

‡: W XANES depicted

n.a.: not available

Table 2c: Electron microprobe analyses of Ni-bearing samples

Sample	Si(wt%)	Al(wt%)	Mg(wt%)	Ca(wt %)	Fe(wt%)	S(wt%)	Ni(wt%)	O(wt%)	Total(wt%)	Edge (eV)
B231205p1 ‡	19.81(8)	6.64(2)	5.14(3)	24.96(2)	0.374(7)	0.214(2)	0.016(2)	42.2(1)	99.3(2)	n.a.
B231205p5	19.8(2)	6.74(5)	5.15(7)	24.82(3)	0.521(4)	0.214(2)	bdl	42.3(2)	99.5(4)	n.a.
B220306p3	19.5(1)	7.22(9)	5.5(1)	24.63(3)	0.10(1)	0.188(5)	0.021(3)	42.3(3)	99.5(7)	n.a.
B070406p6	22.717(8)	8.46(6)	6.5(1)	16.89(8)	0.04(2)	0.058(5)	0.033(2)	44.50(6)	99.2(2)	n.a.
B120406p6 ‡	18.7(9)	6.9(3)	5.3(2)	24.6(2)	0.02(2)	0.022(3)	0.312(9)	41.1(1)	97.3(3)	n.a.
B010806p1 *	20.04(8)	7.00(9)	5.50(5)	25.80(9)	0.04(1)	0.180(4)	0.016(4)	43.2(1)	101.8(3)	2470.5
B010806p2	23.73(4)	8.28(4)	6.47(7)	17.26(3)	0.03(1)	bdl	0.132(8)	45.64(7)	101.7(1)	n.d.
B010806p4	23.6(1)	7.9(2)	6.4(2)	17.37(9)	0.018(7)	bdl	0.091(4)	45.2(2)	100.7(4)	2469
B010806p5	20.1(1)	7.02(1)	5.47(7)	25.53(9)	0.032(9)	0.021(9)	0.10(4)	43.1(2)	101.5(4)	2468.5
B030806p2	20.2(1)	7.04(1)	5.4(1)	25.71(5)	0.05(2)	0.021(8)	0.38(4)	43.2(3)	101.9(6)	n.a.
B030806p5	20.0(1)	6.98(9)	5.4(2)	25.3(2)	0.02(2)	0.016(2)	0.354(5)	42.7(4)	100.7(9)	n.a.
B140906p4 *	20.2(1)	6.96(7)	5.3(1)	25.68(6)	0.08(1)	0.203(3)	0.025(6)	43.2(2)	101.6(5)	2471.2
B140906p5	20.18(9)	7.00(2)	5.28(6)	25.641(8)	0.104(7)	0.199(3)	bdl	43.16(8)	101.6(1)	2471.2
B190906p5	19.8(1)	6.84(8)	5.40(4)	24.1(1)	0.020(5)	bdl	2.473(7)	42.4(2)	101.0(4)	n.a.

\*: S XANES depicted

‡: Ni XANES depicted

n.a.: not available

Table 3: Results of S XANES deconvolution

Sample	Additive	Additive metal (wt %)	S (wt %)	Metal:Ca (molar)	Storage (Days)	P(W)	P(2473.1))	P(2474.9)	P(2476.2)	P(2481.4)	$\chi^2$
B310706p1	Mn	0	0.196	0.0000	113	n.a.	0.11(3)	0.34(7)	0.36(5)	0.19(2)	1.548
B310706p2	Mn	2.07	0.332	0.0606	113	n.a.	0.33(3)	0.21(5)	0.44(4)	0.020(6)	0.355
B310706p3	Mn	3.74	0.48	0.1127	113	n.a.	0.26(3)	0.26(6)	0.36(4)	0.11(1)	0.396
B310706p4	Mn	6.03	0.726	0.1855	113	n.a.	0.31(3)	0.19(4)	0.44(4)	0.06(1)	1.553
B310706p6	Mn	8.74	1.117	0.2852	113	n.a.	0.03(4)	0.22(7)	0.06(4)	0.68(6)	1.124
B151106p1	Mn	0.379	0.229	0.0126	16	n.a.	0.10(3)	0.22(6)	0.27(5)	0.41(5)	0.283
B151106p1N	Mn	0.378	0.229	0.0125	16	n.a.	0.13(4)	0.45(10)	0.40(7)	0.02(1)	0.284
B151106p4	Mn	1.07	0.274	0.0356	16	n.a.	0.19(4)	0.40(9)	0.41(6)	n.a.	0.289
B151106p5	Mn	0.235	0.219	0.0078	15	n.a.	0.15(4)	0.43(9)	0.40(6)	0.03(1)	0.261
B151106p6	Mn	0.84	0.251	0.0281	16	n.a.	0.16(4)	0.44(10)	0.40(7)	n.a.	0.24
B150906p1	W	0.7	0.3	0.0203	70	n.a.	0.14(4)	0.36(9)	0.45(7)	0.05(2)	0.784
B150906p2	W	0.28	0.2	0.0081	70	n.a.	0.15(3)	0.38(8)	0.47(6)	n.a.	1.865
B150906p3	W	0.89	0.206	0.0260	71	n.a.	0.17(4)	0.34(8)	0.46(6)	0.04(1)	0.636
B150906p4	W	0.49	0.202	0.0142	71	n.a.	0.22(3)	0.25(6)	0.52(6)	0.01(2)	1.536
B150906p5	W	0	0.134	0.0000	71	n.a.	0.16(3)	0.34(8)	0.49(6)	n.a.	0.742
B141106p1	W	6.4	0.14	0.0634	11	0.07(1)	0.11(4)	0.3(1)	0.49(8)	n.a.	1.401
B141106p2a	W	2.4	0.1	0.0211	11	0.09(1)	0.13(3)	0.24(7)	0.46(6)	0.09(2)	0.588
B141106p2b	W	2.4	0.1	0.0223	11	0.08(1)	0.07(3)	0.32(9)	0.43(8)	0.10(2)	0.952
B140906p4	Ni	0.03	0.203	0.0008	71	n.a.	0.15(3)	0.38(8)	0.47(6)	n.a.	0.639
B140906p4D	Ni	0.03	0.203	0.0008	71	n.a.	0.29(3)	0.18(5)	0.53(5)	n.a.	0.693
B140906p5	Ni	0.03	0.199	0.0008	71	n.a.	0.21(3)	0.33(7)	0.46(5)	0.001(4)	1.494

n.s.: not significant

P(xxxx) indicates the proportion of the signal accounted for by the peak at xxxx eV

Table 4: Correlation coefficients between peak areas and sample composition for Mn-bearing samples

	Mn	Ca	S	Mn:Ca
	wt %	wt %	wt %	molar
<sup>961</sup> P(2473.1)	0.85	n.s.	0.8	0.84
P(2474.9)	-0.85	n.s.	-0.81	-0.84
P(2476.2)	n.s.	n.s.	n.s.	n.s.

P(xxxx) indicates the proportion of the signal accounted for by the peak at xxxx eV

Table 5: Results of EXAFS fitting. Table headings defined in section 3.3

	n	$E_0$	$r(\text{\AA})$	$\sigma^2$	R factor
Mn	5(1)	6540(4)	2.06(2)	0.009(3)	0.007
W	3(1)	10204(3)	1.77(1)	0.001(1)	0.023
Ni	3.8(9)	8345*	1.96(1)	0.007(4)	0.036

\*: Energy set to maximum first derivative on edge

962

Table 6: Ni pre-edge peak centroid energies

Sample	$E_{\text{pre-edge, sample}} - E_{\text{pre-edge, NiO}}$ (eV)	$1 \sigma$ (eV)
B231205p1	0.48	0.07
B220306p6	0.49	0.05
963 B120406p6	0.56	0.05
B070406p6	0.41	0.16
B190906p5	0.49	0.04
B030806p5	0.5	0.04
B030806p2	0.45	0.05
NiO	0	n.a.



## 8 FIGURE CAPTIONS

964

965 Figure 1: a: Schematic comparison of the transitions that result in the sulphur K edge  
966 for compounds with a greater ionic bonding character, such as MgS, and those with a  
967 greater covalent bonding character, such as FeS; b: Summary of edge positions, defined  
968 as the maximum first derivative, versus oxidation state for standards measured in this  
969 study.

970 Figure 2. S K edge XANES spectra for sulphide standards. Peak at 2481eV indicated by  
971 the dotted line is spurious sulphate caused by oxidation of the samples prior to sample  
972 preparation and analysis. Spectra for CaS and MgS are digitised from Farrell and Fleet  
973 (2000). All other spectra were measured at the NSRRC.

974 Figure 3. S K edge XANES spectra for sulphate standards. All spectra were measured at  
975 the NSRRC.

976 Figure 4. S K edge XANES spectra for selected synthetic silicate glasses. Peak at 2481eV  
977 is spurious sulphate caused by oxidation of the samples prior to sample preparation  
978 and analysis. a: Effect of changes in additive metal on XANES for CMAS (sam-  
979 ple B310706p1), CMAS+Ni (sample B010806p1), CMAS+Mn (sample B310706p2),  
980 CMAS + W (samples B141106p1). b: Effect of changes in additive metal content  
981 on XANES for CMAS+Mn compositions for B310706p3 (3.7 wt% Mn), B310706p4  
982 (6.0 wt% Mn) and B310706p6 (8.7 wt% Mn); c: Effect of changes in sample prepa-  
983 ration method for sample B140906p4. See also Fig. 10c,d; d: Effect of oxidation  
984 state of experiment on S K edge XANES spectra for, from the top down, B020806p2,  
985 B310706p6, B020806p3, B310706p2. Both experiments were performed in the sulphide  
986 stability field. Samples chosen to illustrate the range of sulphate signal produced by  
987 samples from within the same run.

988 Figure 5. Example of results of S XANES peak deconvolution exercise. Thicker line is the  
989 measured XANES. Thin lines are the deconvoluted peak components and fit XANES.  
990 a: B310706p1 (CMAS); b: B310706p4 (CMAS+Mn); c: B141106p2b (CMAS+W).

991 Figure 6. Results of S XANES peak deconvolution exercise. Spectra with proportion  
992 of signal accounted for by the 2481.4 eV (sulphate-related peak) greater than 0.2 and  
993 with low signal:noise are omitted. a: Relationship between the proportion of the signal  
994 accounted for by the peak at 2473.1 eV and the molar Mn:Ca ratio; b: Relationship  
995 between the proportion of the signal accounted for by the peak at 2474.9 eV and molar  
996 Mn:Ca ratio; c: Relationship between the proportion of the signal accounted for by  
997 the peak at 2473.1 eV and W:Ca ratio; d: Relationship between the proportion of the  
998 signal accounted for by the peak at 2476.9 eV and W:Ca ratio.

999 Figure 7. Metal XANES spectra for the metal standards. a: Mn standards; b: W standards;  
1000 c: Ni standards. All metal standards were measured on BL17C at the NSRRC.

1001 Figure 8. Metal XANES spectra for the synthetic glasses. a: Mn K edge spectra in order  
1002 of decreasing Mn:S ratio; b: W L3 edge spectra in order of decreasing W:S ratio. A  
1003 indicates the intense white line, B indicates the post-edge feature discussed in the text;  
1004 c: Ni K edge spectra in order of decreasing Ni:S ratio.

1005 Figure 9. Results of metal EXAFS fitting. R is distance in Angstroms.  $|\chi(R)|$  is the  
1006 magnitude of the Fourier-transformed signal as a function of R. The shape, position  
1007 and size of the peak provides information on the nearest neighbours to the metal probed  
1008 by the EXAFS measurements. Solid line is data, dashed line is the fit. a: average of  
1009 Mn-bearing glasses. b: Average of W-bearing glasses; c: average of Ni-bearing glasses.

1010 Figure 10. Further information on the sulphate peak at 2481.4 eV. a: relationship between  
1011 sample storage duration and the proportion of the signal accounted for by the 2481.4 eV  
1012 peak; b: relationship between sample sulphur content and the proportion of the signal  
1013 accounted for by the 2481.4 eV peak; c: comparison of XANES for the two portions  
1014 of B140906p1 prepared under air and in a nitrogen-filled glovebox. The extension N  
1015 indicates preparation in the glovebox; d: comparison of XANES for the two portions  
1016 of B151106p1 prepared under air and in a nitrogen-filled glovebox. The extension N  
1017 indicates preparation in the glovebox. Dashed line indicates position of sulphate peak.

1018 Figure 11. Comparison of S K edge XANES spectra with sums of sulphide spectra for a:  
1019 B310706p1 (CMAS); b: B310706p6 (CMAS+Mn); c: B141106p1 (CMAS+W).

## 9 FIGURES

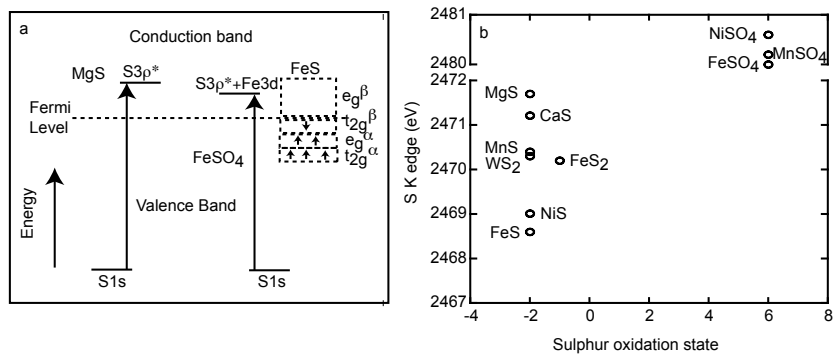


Figure 1:

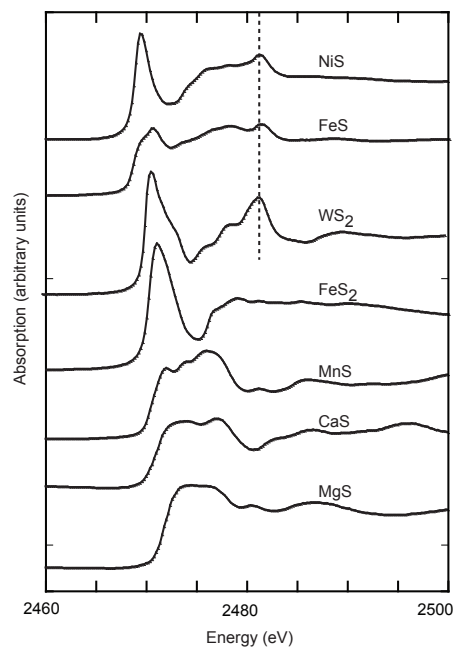


Figure 2:

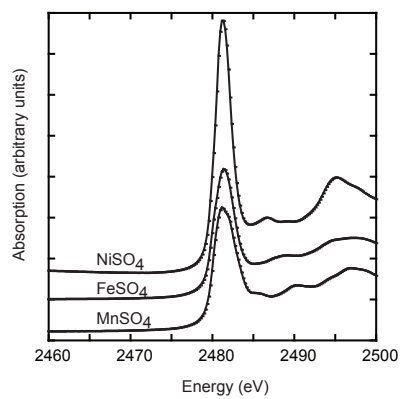


Figure 3:

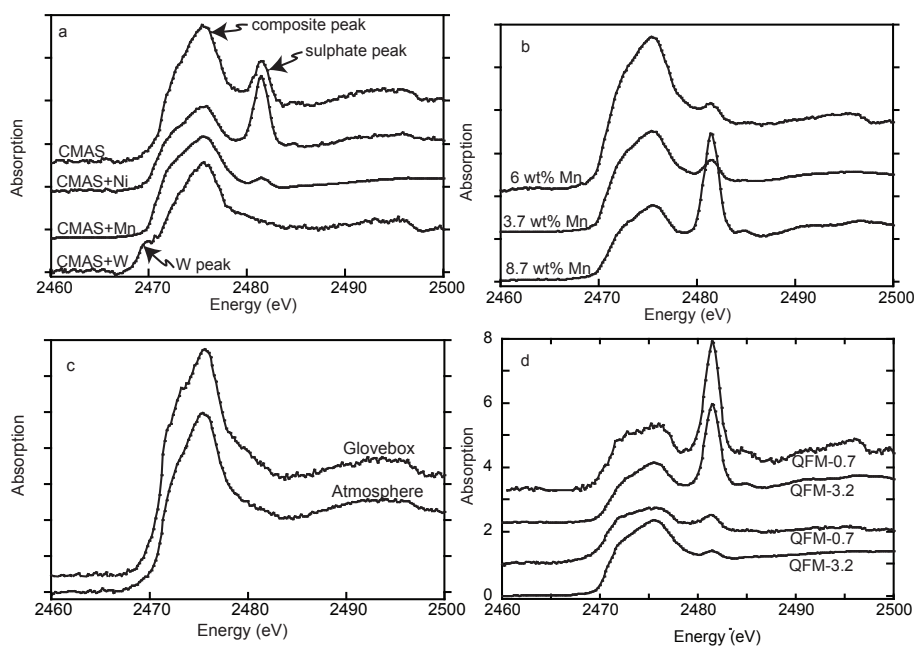


Figure 4:



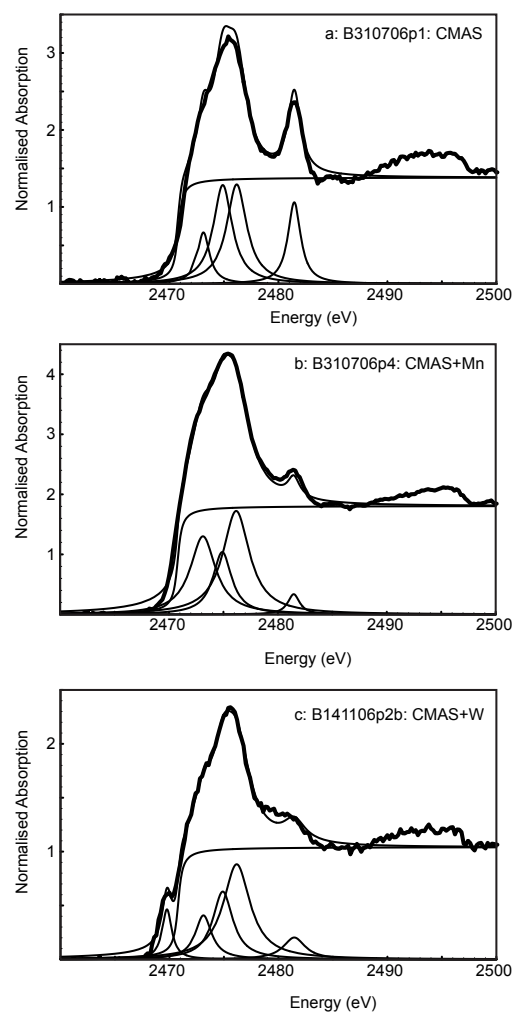


Figure 5:

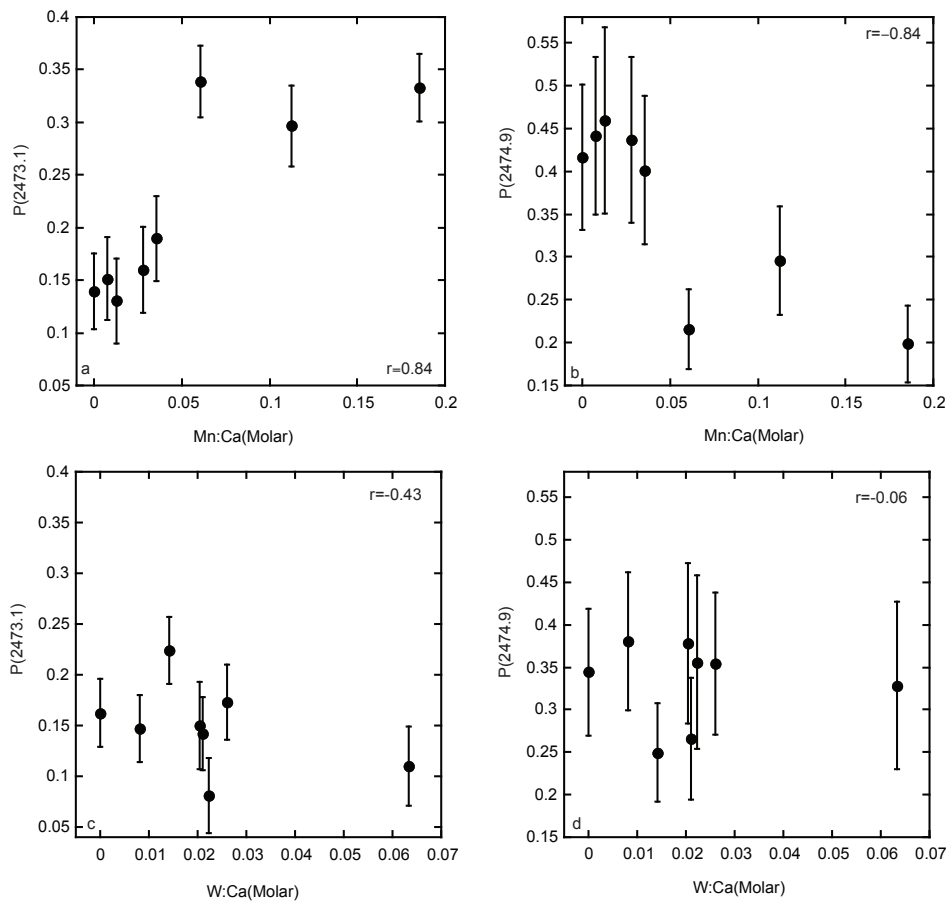


Figure 6:

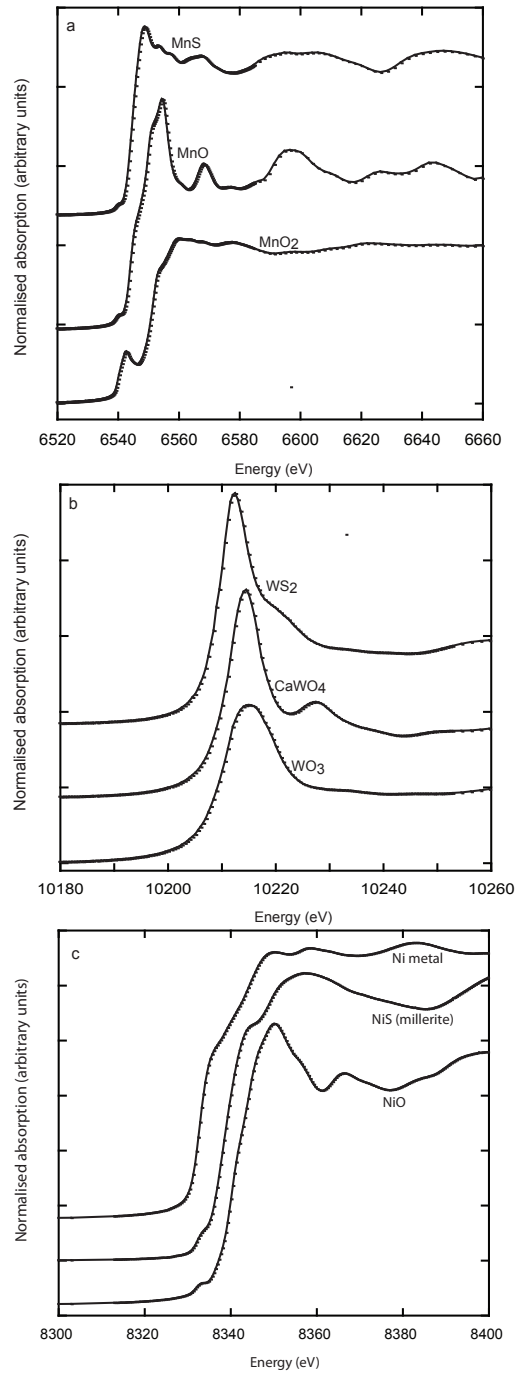


Figure 7:

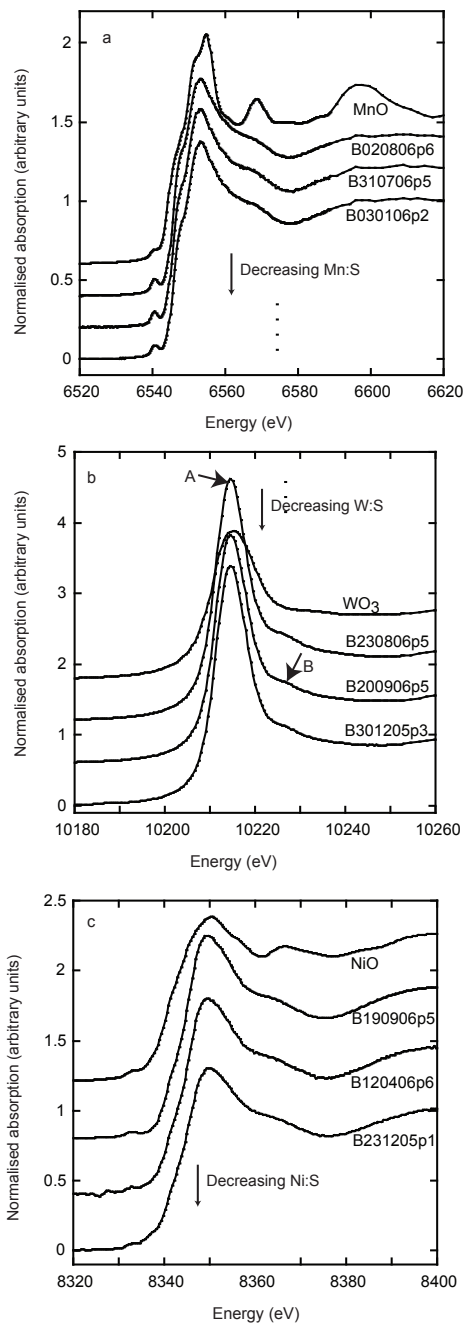


Figure 8:

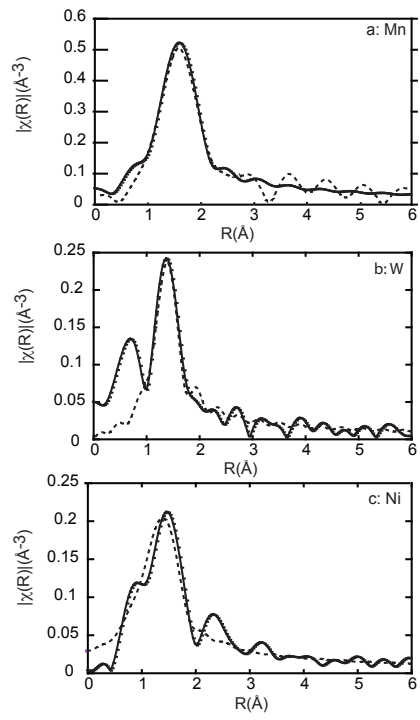


Figure 9:

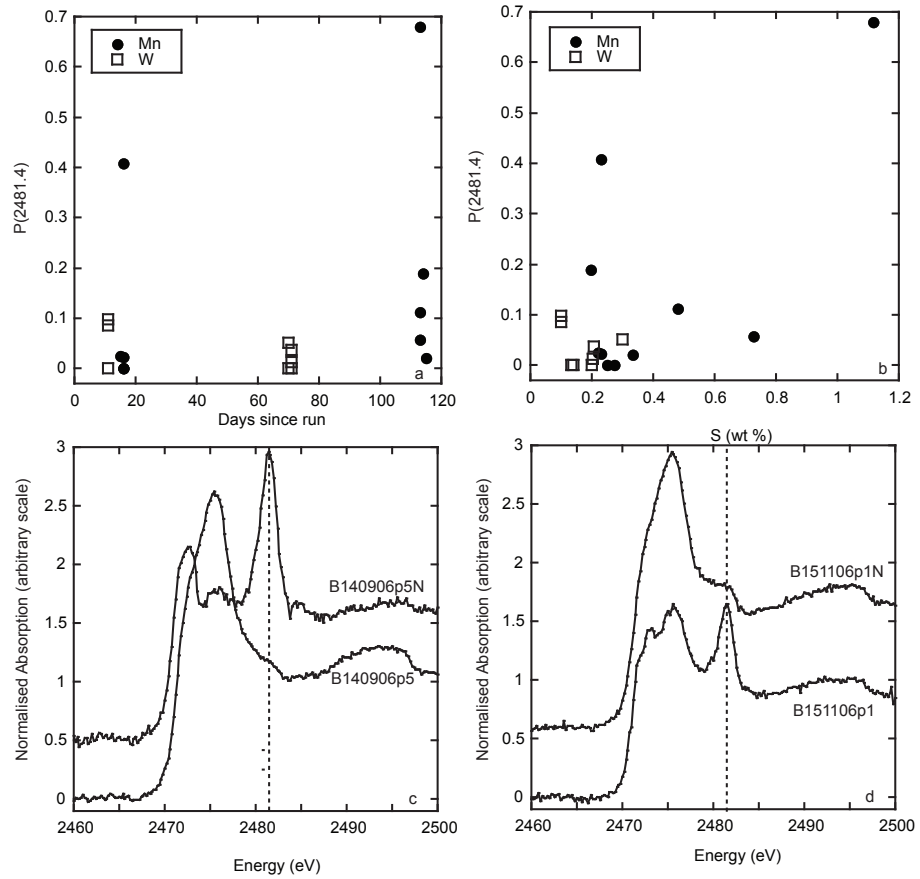


Figure 10:

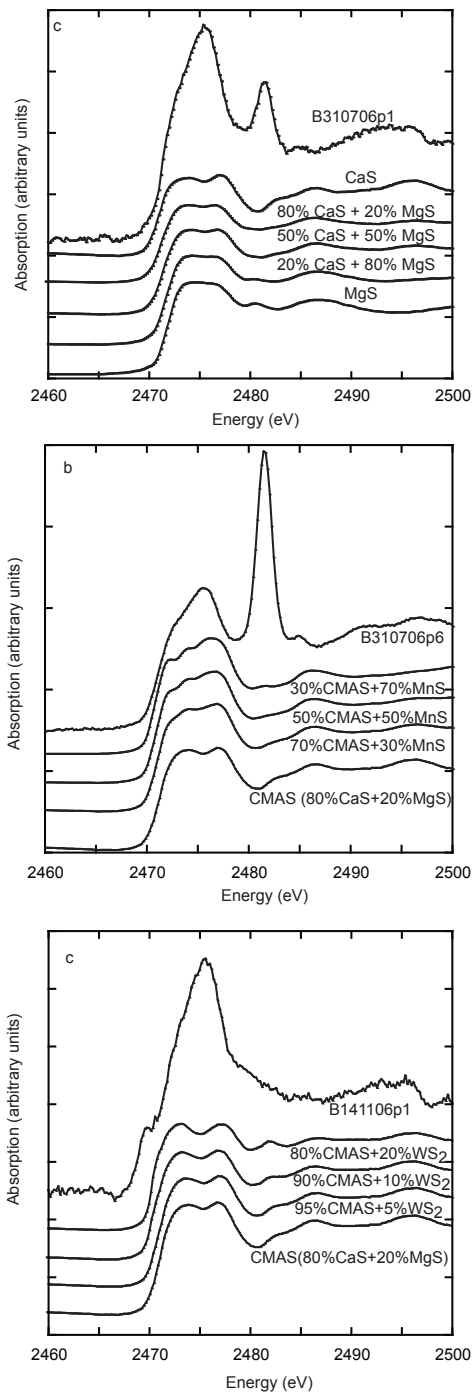


Figure 11: