



In-situ determination of the oxidation state of iron in silicate melts

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Terrestrial lavas commonly contain up to 10 wt % of iron. Furthermore, planetary scientists estimated that the martian mantle has ~18 wt % of iron and rocks returned from the Moon indicate lunar lava containing up to 25 wt % of iron. An experimental challenge in dealing with Fe-bearing silicate melts is that the oxidation state, controlling the proportions of ferric and ferrous iron, is a function of composition, oxygen fugacity and temperature and may vary significantly. Further complications concerning iron originate from its potential to be either four-, six- or even five-fold coordinated in both valence states.

Therefore, the oxidation state of iron was determined in air for silicate melts containing various amounts of iron using XANES method at the Fe K-edge. Investigated samples were Na-disilicate (NS), one atmosphere anorthite-diopside eutectic (AD) and haplogranitic (HPG8) melts containing up to 20, 20 and 10 wt % of iron, respectively. XANES spectra at the Fe K-edge were collected for all the melts at beamline A1, HASYLAB, Hamburg, using a Si(111) four-crystal monochromator. Spectra were collected for temperatures up to 1300 °C using a Pt-Rh loop as heating device. The Fe oxidation state was determined from the centroid position of the pre-edge feature using the calibration of Wilke et al. (2004).

XANES results suggest that oxidation state of iron does not change within error for NS melts with addition of Fe, while AD and HPG8 melts become more oxidised with increasing iron content. Furthermore, NS melts are well more oxidised than AD and HPG8 melts that exhibit relatively similar oxidation states for identical iron con-

tents. The oxidation state of iron for NS melts appears to be slightly temperature-dependent within the temperature range investigated (800-1300 °C). However, this trend is stronger for AD and HPG8 melts. The present in-situ Fe-oxidation states determined for these melts were compared to those obtained on the corresponding glasses quenched from different temperatures, when possible, using wet chemistry analysis (i.e., K-dichromate potentiometry). The wet chemistry analyses indicate a greater amount of Fe³⁺ for all the compositions analysed (i.e., NS, AD and HPG8). These discrepancies in the Fe-oxidation state obtained using both methods (i.e., in the order of 10 %) may stem from the fact that the centroid position of the pre-edge feature was determined using the calibration of Wilke et al. (2004) and this calibration may not be applicable to the present melts. Furthermore, there are considerable differences in the pre-edge intensity between glasses and melts that may be attributed to changes in the local geometry around Fe and they may potentially affect the centroid position determined from the XANES spectra.

References:

Wilke et al. (2004) *Chemical Geology*, 213, 71-87.