

Figure A.1

**Supplementary Figure A.1a-c:** Representative Fe XANES spectra and illustration of the applied fitting procedure. The displayed spectra were collected at the SUL-X beamline at ANKA (Germany). **a)** Full Fe XANES spectra of the reference glasses REV-1, VG568, PD2K3, and AH. A slight fine structure at the main edge crest (near 7140 eV) can be observed for some hydrous glasses (here: REV-1, PD2K3, and AH) but not for the dry glasses (VG568). This is consistent with previous studies (Wilke et al., 2006) and indicates a small change of the Fe coordination in hydrous melts when quenched to a glass. **b)** Illustration of the applied fitting procedure: # background = *exponentially modified Gaussian + arctangent*; \$ fitted spectrum = *background + Gaussian 1 + Gaussian 2*; § residual = *measured spectrum (normalized) – fitted spectrum*. **c)** Fitted pre-edge peaks (after background subtraction) for a sequence of five analyses on the same spot on the rhyolitic reference glass VG568. The width of the cross marking the centroid energy represents the overall uncertainty of the analytical method ( $\pm 0.1$  eV).

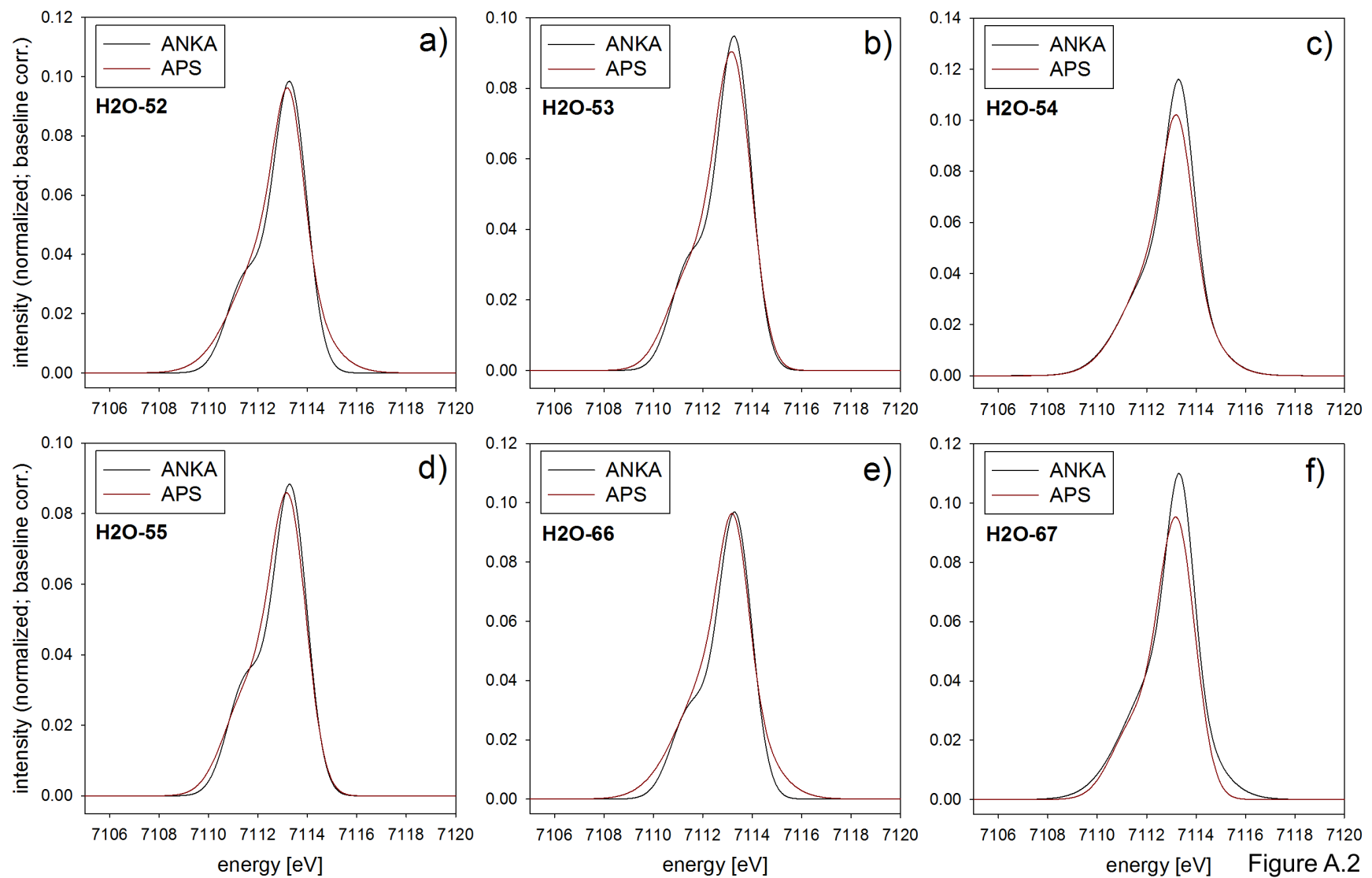


Figure A.2

**Supplementary Figure A.2a-f:** Fe XANES pre-edge peaks of selected rhyolitic reference glass materials measured at APS and ANKA. Details about the references materials (e.g., glass composition, Fe oxidation state and the centroid energy of the pre-edge peak) are given in Table 1 and Supplementary Material B.

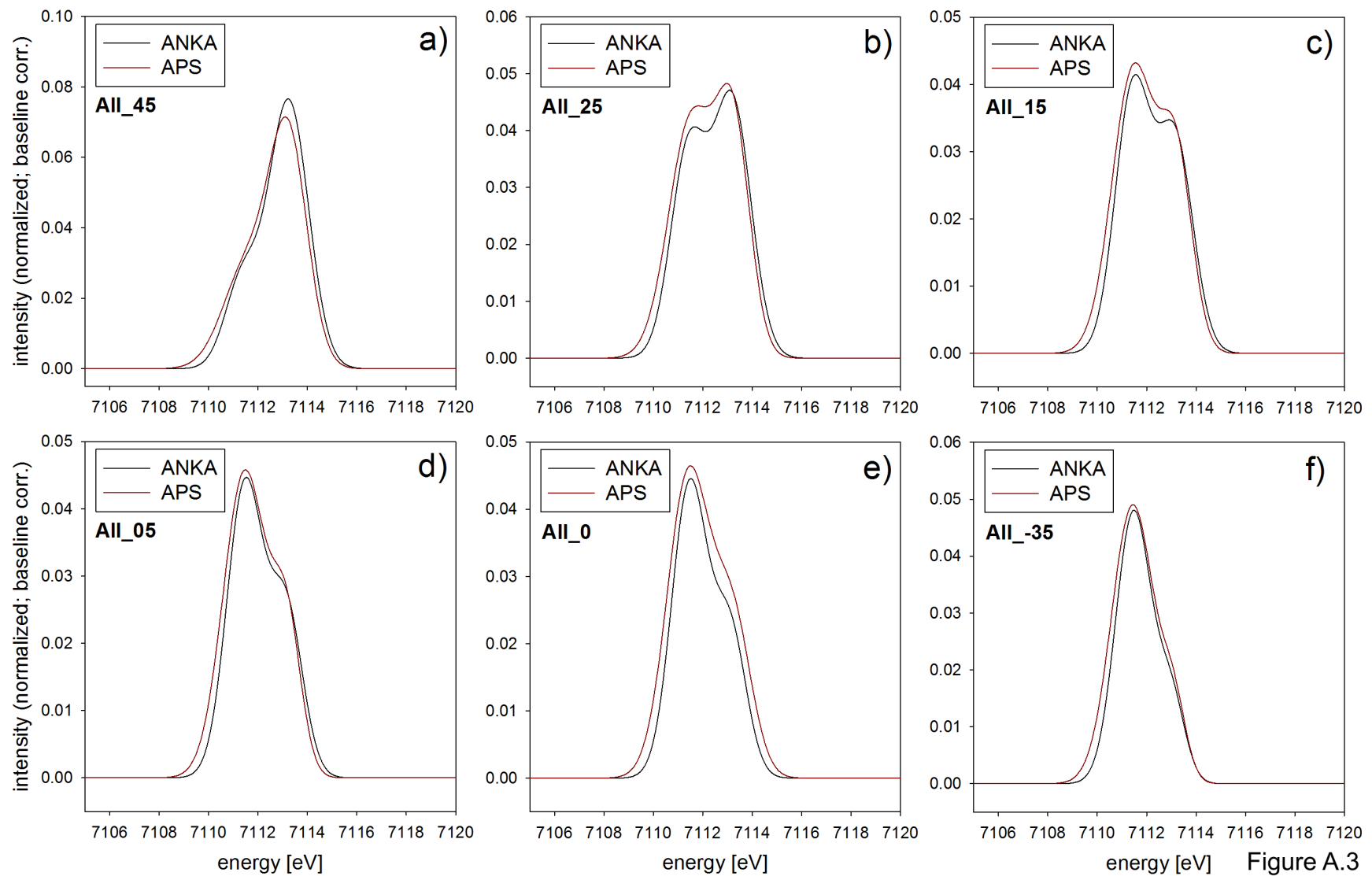


Figure A.3

**Supplementary Figure A.3a-f:** Fe XANES pre-edge peaks of selected basaltic reference glass materials measured at APS and ANKA. Details about the references materials (e.g., glass composition, Fe oxidation state and the centroid energy of the pre-edge peak) are given in Table 1 and Supplementary Material B.

## References

Wilke, M., Schmidt, C., Farges, F., Malavergne, V., Gautron, L., Simionovici, A., Hahn, M., Petit, P.E. (2006). Structural environment of iron in hydrous aluminosilicate glass and melt-evidence from X-ray absorption spectroscopy. *Chemical Geology*, 229, 144-161.