



ESRF

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Medium-range order around iron in natural glasses

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Report: Natural glasses encompass various kinds of Earth materials and particularly volcanic glasses formed during the quench of molten magmas. Volcanic rocks are usually glassy for viscous melts (obsidian glasses) and drastic quench conditions are required to get glasses for more fluid compositions (basaltic glasses). In multicomponent silicate glasses, chemically selective techniques are needed to probe the local environment of specific cations. The chemical selectivity of XAS allows to determine the relationships between cation sites and the glassy network. Iron is one of the major components of most minerals and magmatic liquids. The determination of the sites occupied by ferrous and ferric cations and the connection of the sites with the silicate network in volcanic glasses, give information on cooling conditions as well as on the influence of fluids on the glass/melt structure. However, the sites occupied by ferrous and ferric cations in glasses are still poorly understood due to the complex structure of amorphous materials.

High resolution XANES and EXAFS spectra have been recorded on volcanic glasses at the Fe K-edge using a Si 111 monochromator. The glasses investigated include basaltic compositions (glasses from Hawaii, from the Atlantic mid-ocean ridge) and more differentiated silicic glasses of rhyolitic compositions (obsidians from Mono Crater, California, from Equator and New Mexico). A pre-edge peak is observed on the low energy side of the main edge and is usually assigned to $1s \rightarrow 3d$ like levels transitions. The shape, position and relative intensity of the various components of the pre-edge allow to derive the Fe-coordination number, site distortion and oxidation states. High resolution XANES spectra have also been recorded in crystalline references (iron bearing orthose from Madagascar with 1000 ppm Fe^{3+} , siderite and

ferriphlogopite) and in a synthetic glass ($\text{NaFeSi}_2\text{O}_6$) in order to determine the modification of the pre-edge as a function of Fe crystal chemistry. The influence of the above mentioned parameters on the various pre-edge features has been evaluated on the no noise data presented on figures 1, 2, 3, 4. This set of data, obtained for the first time in volcanic glasses, will be used to discuss the local structure around Fe.

EXAFS Data up to 18 \AA^{-1} have also been recorded. Wide energy range allows to obtain structural information on the medium-range order. The helium cryostat was used down to 10K to get ride of the thermal contribution to the disorder parameter (s). Both transmission and fluorescence mode were used depending on the concentration of iron in the studied glasses or crystalline references.

Figures 1 to 4: High resolution pre-edge recorded using a Sill1 monochromator, a 0.3 eV step and a 4s counting time for each point.

