Non-resonant and resonant X-ray Emission spectroscopy on iron-bearing minerals and glasses

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Iron-bearing minerals and glasses were studied by 1s3p-resonant and non-resonant X-ray emission experiments. Ferrous and ferric minerals were chosen to cover a wide range of possible coordination environments for iron. These data are used to explore the potential for investigating Fe speciation in glasses and melts. Non-resonant $K\beta_{1,3}$ spectroscopy is sensitive to the metal spin state and reflects the effective number of unpaired metal 3d electrons. In resonant emission experiments (1s3p-RIXS), $K\beta_{1,3}$ emission spectra are measured with high resolution while scanning the excitation energy through the absorption edge of the element studied. This provides more detailed information about unoccupied states, particularly allowing separation of weak quadrupolar and strong dipolar transitions. Absorption spectra acquired by partial-fluorescence yield of the $K\beta_{1,3}$-line provide the possibility to acquire XAFS spectra “free” of core-hole lifetime broadening as the spectral resolution in this way is governed by the lifetime of the final state [1],[2].

The experiments have been performed at beamline W1, HASYLAB at DESY, using a Si(111) double-crystal monochromator (resolution of ca. 1.5 eV at 5 keV). The emission spectra were recorded using an in-vaccuum crystal spectrometer in Rowland-circle geometry [3]. Spherically bent Si(440) and Si(531) were used as analyzer. Emitted photons were detected
by a CCD camera, which was used as a position sensitive detector.

For the minerals, slight but significant shifts of the $K\beta_{1,3}$-peak to lower energies are observed between Fe^{2+} and Fe^{3+} at constant coordination. However, the comparison of all spectra indicates that there is no simple relationship between $K\beta_{1,3}$ spectra and the iron oxidation state. Instead, it is obvious that the crystal or ligand field has a non-negligible effect, which may counterbalance the one induced by the oxidation state. For Fe in oxidized and reduced basaltic glasses, the $K\beta_{1,3}$-emission spectra display only very subtle differences in the position of the peak maximum and more significant differences in the width and position of the Kβ’ peak. The only very small differences in the spectra can be explained by the fact that the coordination of Fe in silicate glass and melt changes with oxidation state from 5/6-fold for Fe^{2+} to tetrahedral for Fe^{3+}, which appears to have counterbalancing effects for the $K\beta_{1,3}$-emission spectra. The pre-edge region of the Fe K-edge probes transitions from 1s to the 3d level, which are of quadrupolar nature for centro-symmetric and dipolar for non-centro-symmetric Fe sites. These excitations can be analyzed using the 1s3p-RIXS plane, which corresponds to $K\beta_{1,3}$-emission spectra collected at excitation energies of the pre-edge region. Profiles through this plane at constant excitation energies (CIE-profiles) provide information similar to Fe M-edge absorption spectra [1]. The peak of CIE-profiles shifts by about 1.5 eV between fayalite and hematite (6-fold coordinated Fe). In addition, the spectrum of fayalite displays a fine structure that is probably related to crystal field effects. The maxima of the CIE-profiles of the reduced and oxidized basaltic glasses also display a shift of ca. 1.5. eV and may exploited for measurements of the Fe oxidations state.

References:
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