

Iron Speciation Microanalysis: Evaluating Low Overvoltage Wavelength Dispersive Spectrometry Using Natural Reference Materials

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Determining the ratio of Fe²⁺/Fe³⁺ in solids has traditionally been performed by a variety of methods: 1) bulk analysis by Mössbauer spectroscopy [1], millimetric analysis by X-ray photoelectron spectroscopy [2], or microbeam analysis at high spectral resolution by X-ray absorption spectroscopy (XAS) using a synchrotron light source [3,4]. While XAS produces high fidelity results, it suffers from additional overhead, e.g. preparing a proposal, travel to the light source, and the restrictions imposed by the limited time allotted for an approved study. Wavelength dispersive (WD)-based X-ray emission spectrometry in the electron microprobe has also been employed to characterize the chemical state of iron [5-7], as well as determining Fe concentration at higher spatial resolution using non-conventional L-lines [8].

Previous EPMA studies emphasize the significant correction required for Fe L line data owing to self-absorption of Fe L_α and L_β X-rays by the L₃ and L₂ edges. Because of the nature of the electron beam interaction volume, the magnitude of this correction scales with beam energy. Accordingly, we have collected Fe L WD spectra using accelerating voltages as low as 2 keV for a number of Fe-bearing reference materials, including: hematite (Fe₂O₃), magnetite (Fe₃O₄), fayalite (Fe₂SiO₄), ilmenite (FeTiO₃), and pyrite (FeS₂). The emergence of field emission EPMA's over the past 8-9 years has made the use of overvoltages (E₀/E_c) of 2.9 possible for Fe L_α (705 eV) using a 2 keV beam. One goal of this study was to determine if the lowest practical beam voltages could be used to evaluate the Fe²⁺/ (Fe²⁺+Fe³⁺) proportion in natural basaltic glasses (e.g. VG2) where the ratio has been previously characterized by wet chemistry to be 83% [9]. Fe L spectra have been deconvolved using a sum of Gaussian and Lorentzian peak shapes, resulting in fits with r² values between 0.97-0.99, for the fewest number of peaks required to describe the data. Our initial results collected at 2 keV show that the peak centroid for Fe L_α in VG2 (24% Gaussian peak shape) is shifted by less than an eV relative to Fe³⁺ (Fe₂O₃: 39% Gaussian) and indistinguishable from Fe²⁺ (fayalite: 45% Gaussian) (Figures A-C). Data collected at 5 keV suffer significantly greater self-absorption and are shown for reference (Figures A'-C'). A new method for treating WDS spectra when fitting compound Gaussian and Lorentzian peaks shapes will be proposed.

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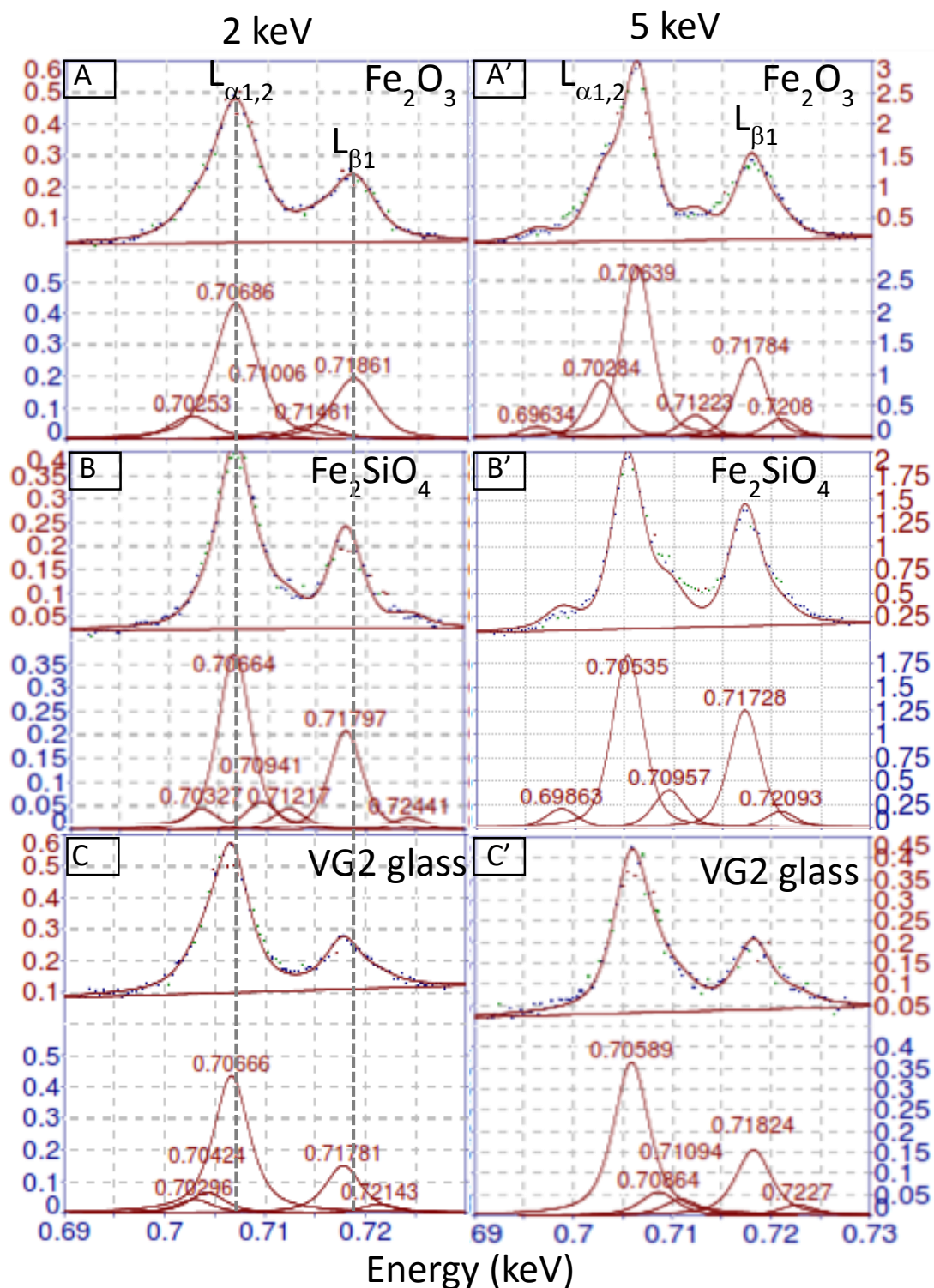


Figure 1. A, B, and C) Iron L line WDS scans for Fe_2O_3 , Fe_2SiO_4 , and VG2 glass at $E_0 = 2$ keV; A', B', and C') Iron L line WDS scans for Fe_2O_3 , Fe_2SiO_4 , and VG2 glass at $E_0 = 5$ keV.