

IN SITU DETERMINATION OF $Fe^{3+}/\Sigma Fe$ OF SPINELS BY ELECTRON MICROPROBE: AN EVALUATION OF THE FLANK METHOD. J. Berlin¹, M. Spilde², A. J. Brearley¹, D. S. Draper² & M. D. Dyar³. ¹Department of Earth & Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, U.S.A., ²Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, U.S.A., ³Department of Earth and Environment, Mount Holyoke College, South Hadley, MA 01075, U.S.A., E-mail: jberlin@unm.edu

Introduction: In the past decade, progress has been made in the *in situ* determination of $Fe^{3+}/\Sigma Fe$ ratios of minerals (which can be used to infer oxygen fugacity, fO_2) with techniques such as TEM-EELS, Mössbauer milliprobe, and microXanes [1-3]. In addition, electron microprobes can measure the intensity change and shift of the L lines with the oxidation state of iron [4-7]. We are currently investigating potential applications of the Flank method [4-6] to geologic problems. Our goal is to evaluate whether the Flank method can be used to detect variation of $Fe^{3+}/\Sigma Fe$ (and hence fO_2) in spinel grains from terrestrial mantle xenoliths.

Technique: The Flank method [4-6] uses the differences between Fe L line spectra of Fe oxides with varying oxidation states (wüstite, magnetite, hematite) which are most pronounced on the low energy flank of the Fe $L\beta$ line and on the high energy flank of the Fe $L\alpha$ line. When X-ray intensities are determined at fixed wavelengths on the flanks of the $L\alpha$ and $L\beta$ peaks, the $L\beta/L\alpha$ intensity ratios are inversely correlated with the $Fe^{3+}/\Sigma Fe$ ratios for the three pure Fe oxides. For these phases, an error as small as 0.02 for the $Fe^{3+}/\Sigma Fe$ ratio is obtained [4]. However, for more complex minerals, matrix effects (chemical bonding and composition) affect the $L\beta/L\alpha$ ratio dramatically. To account for these matrix effects and before the method can be applied to minerals with unknown $Fe^{3+}/\Sigma Fe$ ratios, working curves need to be established as was done for synthetic garnets by Höfer & Brey [6].

Samples: In order to investigate if a Flank-method calibration curve for spinels can be established, we are using samples with $Fe^{3+}/\Sigma Fe$ ratios that have been determined previously by Mössbauer spectroscopy on bulk spinel separates. These include spinels from the Simcoe volcano, Washington [8], Cima and Dish Hill, California as well as from Harrat al Kishb and Harrat Hutaymah, Saudi Arabia. The Simcoe spinels have similar bulk compositions ($Mg\# = 69.0-72.4$, $Cr/Cr+Al = 31.9-34.5$) and range in $Fe^{3+}/\Sigma Fe$ from 27 to 38. The other spinels show a wide range of compositions ($Mg\# = 70.0-78.6$, $Cr/Cr+Al = 9.8-32.2$) and have $Fe^{3+}/\Sigma Fe$ from 12 to 37.

We are also analyzing xenolith samples from the Puerco Necks, New Mexico, for which Mössbauer data have not been obtained yet. Spinel in these samples is especially likely to have variations of $Fe^{3+}/\Sigma Fe$ on the microscopic scale as they show compositional zoning

in addition to exhibiting a wide range of colors (brown, black, green, and purple).

Preliminary results: The calibration of the Flank method for spinels is complicated by many factors such as the huge range of compositional, structural, and bonding effects which can change the shape of the Fe L lines. In addition, instrumental parameters such as spectrometer reproducibility [5] and stability of the beam current during the measurements need to be monitored carefully. Keeping the beam current constant (50.0 ± 0.2 nA), we have found significant variations in the shapes of Fe L spectra taken on single spinel grains of Puerco neck xenoliths (Fig. 1). However, these variations are not systematic in a way that would imply core-to-rim zoning in $Fe^{3+}/\Sigma Fe$ and thus fO_2 .

Acknowledgements: We are grateful to A. Brandon and J. Selverstone, who are providing samples for this study.

References: [1] Garvie L. A. J. & Buseck P. R. (1998) *Nature* **396**, 667-670. [2] Sobolev V. N. et al. (1999) *Am. Min.* **84**, 78-85. [3] Delaney J. S. et al. (1998) *Geology* **26**, 139-142. [4] Höfer H. E. et al. (1994) *Europ. J. Min.* **6**, 407-418. [5] Höfer H. E. et al. (2000) *Europ. J. Min.* **12**, 63-71. [6] Höfer H. E. & Brey G. P. (2001) *11th Ann. Goldschmidt Conference*, # 3227. [7] Fialin M. et al. (2001) *Am. Min.* **86**, 456-465. [8] Brandon A. D. & Draper D. S. (1996) *GCA* **60**, 1739-1749.

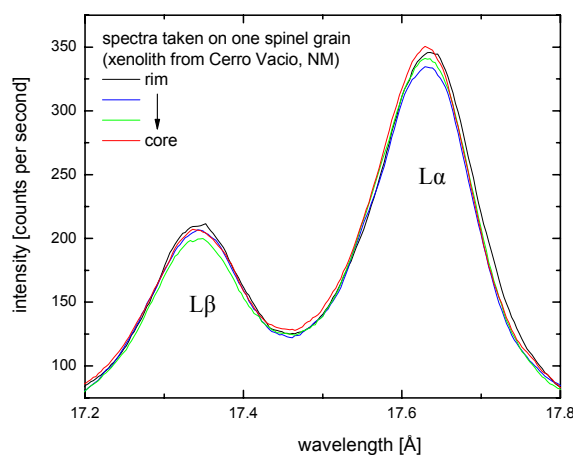


Fig. 1: Fe L emission spectra taken on one spinel grain in a xenolith sample from Cerro Vacio, NM (10 keV, 50 nA, TAPJ crystal). The spectra are smoothed.