

X-RAY STANDING WAVE BASED INTERNAL REFERENCE METHOD FOR QUANTIFICATION OF IMPLANTED FE IN GENESIS SAMPLES. K. Kitts¹, Y. Choi^{1,2}, P. Eng², and S. R. Sutton², ¹Department of Geology & Environ. Geosciences, Northern Illinois University (Davis Hall 312, Normal Rd, DeKalb, IL 60115; kkitts@niu.edu), ²GSECARS, University of Chicago, Argonne, Illinois, 60439.

Introduction: NASA launched the Genesis Return Mission to obtain pristine solar wind. Unfortunately, the probe crash-landed necessitating the application of non-destructive methods that allows the differentiation of both the terrestrial contamination and low concentration solar wind from the substrate. Such techniques include x-ray standing wave (XSW) analysis, x-ray reflectivity and x-ray fluorescence (XRF). When combined, these methods allow the measurement of elemental depth distributions to determine absolute solar wind elemental abundances [1, 2].

In typical quantitative XSW analysis, a separate standard of known concentration is required for calibration. Similarly, we compare measured XSW results from a Genesis sample and an Fe implanted standard in order to obtain Fe abundance from the Genesis sample. Additionally, we present an internal reference approach based on grazing incidence XSW for quantifying the absolute concentrations of trace elements in Genesis substrates eliminating the need for a separate standard. We calibrate the depth profile of the target trace element by comparing fluorescence intensities between the reference element in the substrate and the trace element. We demonstrate the robustness of our method by comparing it directly to the implant standard method under identical experimental conditions and present the absolute Fe solar wind abundance in Genesis sapphire 50722.

Experimental Design: These experiments were performed at 13-ID-C of the GeoSoilEnviro Consortium for Advanced Radiation Sources at the Advanced Photon Source at Argonne National Lab using the experimental set-up described in [2]. Grazing incidence makes use of the interference between incoming and outgoing grazing x-rays resulting in enhanced electric field intensity variations localized near the surface [3, 4]. By measuring the angular dependence of the fluorescence of the implanted elements and taking advantage of the localized electric field enhancement due to this interference, depth profiles and subsequently quantitative elemental abundance of implanted ions can be determined. The fluorescent yield for a particular element as a function of incident angle θ is given by:

$$Y(\theta) = F \int_{z_{\min}}^{z_{\max}} I(\theta, z) N(z) e^{-z/l_a} G(\theta) dz \quad (1)$$

where $N(z)$ is the abundance depth profile of the fluorescing element, l_a is the attenuation length of the out-

going fluorescence, and $I(\theta, z)$ is the electric field intensity at depth z and angle θ and is based on the specular reflectivity. F is an x-ray energy-, element-, and setup-dependent factor used to scale the data and is identical for the Genesis and implanted standard measurements within the comparison approach. $G(\theta)$ is a footprint correction that accounts for the x-ray beam footprint change with θ . The electric field intensity profile $I(\theta, z)$ is calculated using Parratt's recursive formalism with the parameters obtained from the reflectivity fits [5, 6].

Results-Standard Approach: Using this methodology and performing the standard implant calibration, we measured a Genesis sapphire sample (50722) and an Fe-implant (5×10^{14} Fe/cm²) made from a matching flight spare. The results appear in Fig. 1, which compares the measured reflectivity (top panels) and Fe K α fluorescence (bottom panels) of both the Genesis (a) and Fe-implant standard (b). The Genesis sample (lower panel) exhibits significant Fe XRF signal below the critical angle for total external reflection (θ_c) whereas the implanted standard (lower panel) does not. Since the depth of x-ray penetration into the sapphire surface below θ_c is small (< 40 Å), the observed Fe XRF below θ_c indicates that there are Fe atoms above or at the reflecting sapphire surface. These Fe atoms most likely originate from terrestrial surface contamination. By using Eq. 1 and fitting the depth profile $N_{Fe}(z)$ of the Fe atoms to the Fe XRF data in Fig. 1 (solid line), the Fe distribution can be quantitatively determined.

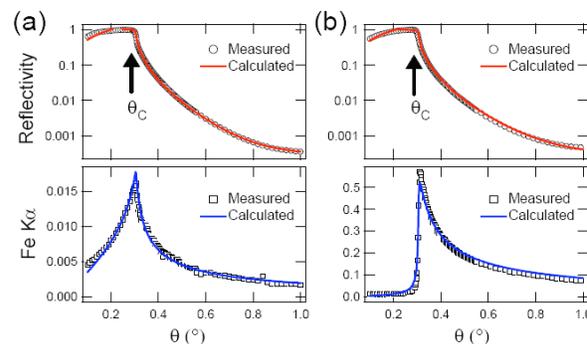


Fig. 1. Reflectivity and Fe K α fluorescence curves from the Genesis sample 50722 (a) and the standard (b).

Figure 2 shows the $N_{Fe}(z)$ profiles resulting from the XRF profile fits in Fig. 1. In Fig. 2a, the terrestrial surface contamination (sharp peak) is clearly resolv-

able from the implanted solar wind (the weaker broad feature and inset). In contrast to the Genesis sample, the implant standard (Fig. 2b) shows only a smooth Fe distribution below the surface. The fitted distribution is in good agreement with the ion implanted simulation calculation (SRIM code) [7] shown as the inset in Fig. 2b. The known fluence of the standard and the area under the profiles (A1 and A2 in Fig. 2) were used to quantify the Fe concentration within the Genesis sample as $(A1/A2)5 \times 10^{14} \text{ Fe/cm}^2$. The resulting Genesis Fe fluence is $1.6 (\pm 0.4) \times 10^{12} \text{ Fe/cm}^2$ with the error determined from the variance of the fit. However, systematic errors resulting from the use of a standard are difficult to quantify.

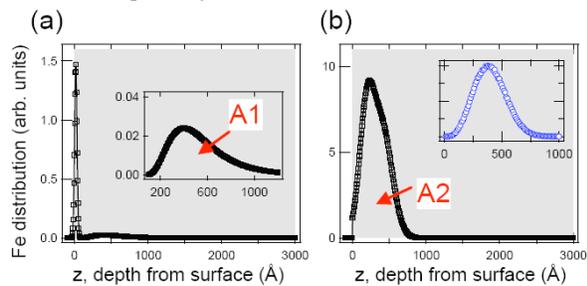


Fig. 2. Fitted Fe distribution, $N_{\text{Fe}}(z)$, as a function of depth for the Genesis 50722 (a) and the standard (b).

Results-New Internal Reference Approach: Due to its crystal structure and stoichiometry, the number of Al atoms per unit volume in the Al_2O_3 substrate can be calculated ($4.690 \times 10^{22} \text{ Al/cm}^3$). Since the electric field intensity variation and attenuation length for the outgoing fluorescence can be readily obtained, the fluorescence intensity from substrate elements can be used as an internal standard to calibrate the fluorescence intensity from an element of interest.

For absolute quantification, there are additional factors that need to be addressed and for simplicity are folded into the F in Eq. 1. However, we list them here as due diligence. Specifically, the detected fluorescence intensities $I(\text{Al-K}\alpha)$ and $I(\text{Fe-K}\alpha)$ are proportional to the element-dependent and incident-energy-dependent cross-section $\sigma(E_0)$, the fluorescence yield ω_K , the transmission ratios from the sample surface to the detector, and the detector efficiency. The first two, $\sigma(E_0)$ and ω_K , are well tabulated for non-resonant energies [8, 9] allowing comparative analysis between trace and substrate fluorescence intensities. The attenuation inside the sample is already included in Eq. 1. For each fluorescence emission, the different transmission rate from the sample surface to the fluorescence detector can be determined as the distance and materials between them are known.

Figure 3 shows the data obtained from the Genesis sample (50722). Figure 3a shows the measured and

fitted reflectivity curves. Figure 3b shows the measured and fitted Fe K α fluorescence profiles. Figure 3c shows the Al K α fluorescence from Al in the Al_2O_3 substrate. Figure 3d shows the fitted Fe distribution. From these data, the solar wind Fe fluence obtained is $1.6 (\pm 0.2) \times 10^{12} \text{ Fe/cm}^2$. Comparing this with the results in Figures 1 and 2, it is clear that the internal reference approach produces consistent results and has the additional value of reducing the need to measure a separate standard thereby reducing the uncertainty.

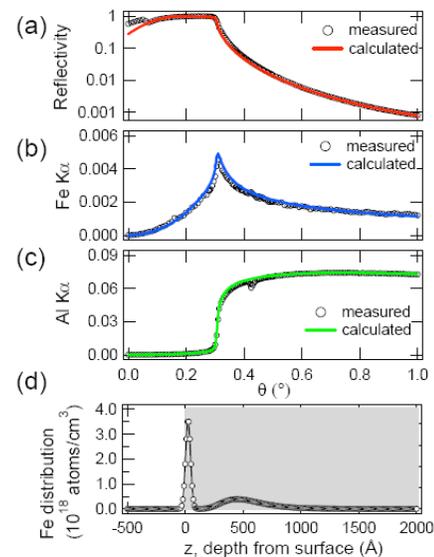


Fig. 3. Genesis 50722 (a) Reflectivity. (b) Fe K α fluorescence. (c) Al K α fluorescence. (d) Fitted Fe distribution.

Conclusion: We have determined that the Fe implanted solar wind absolute abundance in 50722 is $1.6 (\pm 0.2) \times 10^{12} \text{ Fe/cm}^2$. Ongoing secondary ion mass spectrometry analysis [10] of other Genesis samples are in the range of 1.4 to $1.8 \times 10^{12} \text{ Fe/cm}^2$. This new internal self-referencing technique reduces many of the systematic errors inherent in using separate standards.

References: [1] Kitts et al., (2008) *LPSC Abstr.*, **39** #1296. [2] Kitts et al., (2006) *LPSC Abstr.*, **37**, #1451. [3] Becker and Golovchenko, (1983) *Phys. Rev. Lett.* **50**, 153. [4] Bloch et al., (1985) *Phys. Rev. Lett.* **54**, 1039. [5] Parratt, *Phys. Rev.* (1954) **95**, 359. [6] de Boer, *Phys. Rev. B* (1991) **44**, 498. [7] Ziegler et al., (2008) SRIM, (www.srim.org). [8] Chantler, (1995) *J. Phys. Chem. Ref. Data* **24**, 71. [9] Chantler, (2000) *J. Phys. Chem. Ref. Data* **29**, 597. [10] D. Burnett, private communication (unpublished).

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