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doi:10.1017/S1431927621009065
Microsc. Microanal. 27 (Suppl 1), 2021

Compositional Analysis of Chondritic Sulfide Material: A Test of the Mass-Thickness Approach to Quantitative EDS in the TEM

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Energy-dispersive X-ray spectroscopy (EDS) is central to the compositional analysis of planetary materials. When coupled to a transmission electron microscope (TEM), EDS can provide both qualitative and quantitative information in the form of false-color maps and as (normalized) elemental abundances, respectively, at scales ranging from the micrometer down to the atomic. Such information is important in planetary science for identifying two-dimensional compositional variations and as an aid to phase identification. Quantitative information is particularly important for comparing material composition to the output of thermodynamic codes as part of the process of reverse engineering the origins and history of planetary materials and parameterizing chemical models of the early solar nebula. Thus, quantitative EDS has been a mainstay tool of the planetary-science community for decades and will continue to be important for analysis of samples we currently have in our collections and those returned by sample-return missions such as Hayabusa2 [1] and to be returned by OSIRIS-REx [2].

There are several approaches to quantitative EDS in the transmission electron microscope (TEM). Briefly, the 'Cliff-Lorimer (CL) approach' [3] has arguably been the most widely used method. By assuming a 'thin-foil criterion', i.e., that the sample is sufficiently thin so photoelectric absorption and secondary fluorescence effects can be neglected, the intensity of characteristic peaks is proportional to the elemental concentration multiplied by a detector sensitivity 'k' factor, determined by measuring reference standards specific to the element of interest. With sufficient counting statistics, 1% relative error is achievable. The CL approach is suitable for thin specimens but becomes problematic for thicker samples, where absorption and secondary fluorescence can become significant. In comparison, the ζ-factor method utilizes pure element thin-film standards to derive a ζ-factor assuming X-ray yield is proportional to mass thickness [4]. However, this approach requires measurement of beam current, which in turn, requires a sample holder with an integrated Faraday cup. Recently, [5] reported a new approach involving a single standard, known as M^2T. A single thin film with known mass thickness serves as a reference without the need to measure beam current. This mass-thickness approach potentially offers a robust means of quantitative analysis without prior knowledge of beam current and an alternative method to EELS for determination of sample thickness. We previously explored this mass-thickness approach to the analysis of synthetic and natural perovskites, $SrTiO_3$ and $CaTiO_3$, respectively [6]. Here we expand on that effort with application to chondritic Fe-sulfide materials.

We used a Si_3N_4 mass-thickness standard for a beam measurement, which establishes the expected X-ray yield under a standard set of optical and detector conditions. Our Si_3N_4 sample was measured using a 200 kV aberration-corrected Hitachi HF5000 scanning TEM (S/TEM) located in the Kuiper Materials Imaging and Characterization Facility (KMICF) at the University of Arizona (UA), and equipped with an Oxford Instruments X-MaxN 100 TLE EDS system with dual 100 mm^2 windowless silicon-drift detectors running AZtecTEM software. The beam measurement was performed over a large (>250 nm) area until a total of 600,000 counts were acquired in the spectrum. The measurement was repeated to verify beam-current stability within 2% of the initial value. In addition to our Si_3N_4 reference, we measured sulfide material extracted from the Saint-Séverin LL6 chondritic meteorite. The assemblage (Mx4 OA5; Matrix area 4, Opaque Assemblage 5) was described in detail and measured for its composition via quantitative wavelength-dispersive spectrometry using electron microprobe analysis (EMPA) by [7]. Briefly, the pyrrhotite-pentlandite assemblage is 71 × 54 μm in size (orthogonal dimensions) and contains a subhedral morphology. Occurring

within the assemblage is a 57 × 54 μm wide grain of pyrrhotite (Fe,Ni,Co,$Cr_{1-x}S$ where $0 \leq x \leq 0.2$) and a 29 × 28 μm wide grain of pentlandite [$(Fe,Ni)_9S_8$]). We extracted a section from Mx4 OA5, transecting the pyrrhotite and pentlandite interface, and thinned it to electron transparency using a ThermoScientific (formerly FEI) Helios G3 focused-ion-beam scanning-electron microscope (FIB-SEM), also located in the KMICF at UA, with previously described methods [8]. We acquired spectrum images from the FIB section in scanning TEM (STEM) mode using a 100 pm probe size with the sample tilted 10° clockwise about the sample-rod axis (α tilt) toward the right detector (the left detector was turned off).

Figure 1 shows an annular-dark-field (ADF) reference image of part of the FIB section from Mx4 OA5 together with corresponding EDS maps. The interface between the pyrrhotite and pentlandite is visible in the ADF image and the Fe and Ni K series maps. We extracted summed spectra from rectangular regions (~1 × 2 μm) in the pyrrhotite ('Spectrum 1') and pentlandite ('Spectrum 2'). The spectra show that the pyrrhotite contains Fe and S, whereas pentlandite contains Fe, S, and Ni with minor Co. After background removal and deconvolution of artifact peaks, e.g., Cu from the TEM half grid, we quantified the spectra. Table 1 shows the quantification of the pyrrhotite and the pentlandite from the STEM data as well as their compositions measured initially by EMPA. The data show that the quantification of the STEM-EDS spectra using the mass-thickness approach is within 2 wt% of the average composition measured by EMPA. We conclude that the mass-thickness approach to EDS is a viable single-standard technique for quantifying the composition of planetary materials.

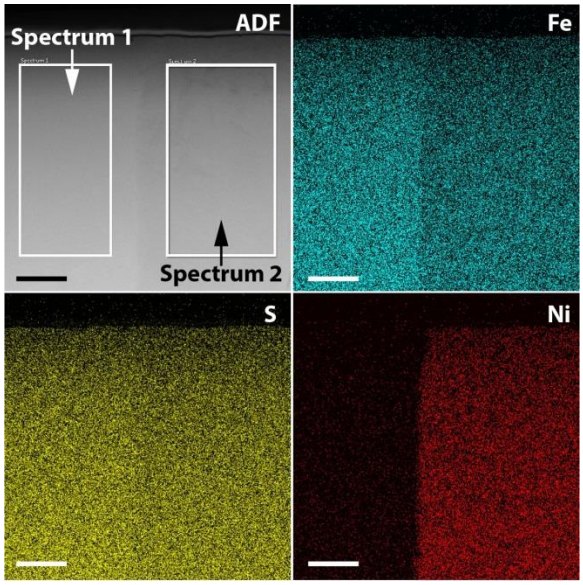

Figure 1. Figure 1. STEM-EDS data on Saint-Séverin FIB section from Mx4 OA5. The annular dark field (ADF) reference image is shown together with the Fe, S, and Ni Kα EDS maps. Scale bar equals 50 nm.

https://doi.org/10.1017/S1431927621009065 Published online by Cambridge University Press

Spectrum 1 - Pyrrhotite			
Element	**Wt%**	**Average Wt% from EMPA [7]**	**Wt% Range from EMPA [7]**
S	38.14	36.8	36.1 - 37.8
Fe	61.86	63.1	61.8 - 64
Total	100	99.9	

Spectrum 2 - Pentlandite			
Element	**Wt%**	**Average Wt% from EMPA [7]**	**Wt% Range from EMPA [7]**
S	34.46	33.7	33.1 - 34.2
Fe	45.75	43.7	40.9 - 46.2
Co	0.98	0.85	bdl - 2.41
Ni	18.81	20.4	17.2 - 23.1
Total	100	98.65	

Figure 2. Table 1. Quantified EDS data from summed 'Spectrum 1' and 'Spectrum 2' shown in Fig. 1. Bdl = below detection level. Totals for microprobe data shown as averages and are within error of 100%.

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