

B, C, N and O analysis by EPMA-SXES

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Measurement of the light elements boron, carbon, nitrogen and oxygen by electron probe microanalysis (EPMA) has consistently been fraught with challenges due to low count rates, poor peak-to-background ratios, X-ray peak shape and position changes in reaction to bonding environment and crystallographic structure, interferences caused by higher-order X-ray lines, inadequate matrix correction procedures, and problems associated with beam damage and hydrocarbon contamination during analysis. The introduction of layered synthetic microstructure (LSM) crystals in the late 1970's drastically increased peak intensities for these light elements compared to previously available stearate (STE) crystals (up to 50x depending on crystal type and analytical conditions). However, LSM crystals also resulted in substantially broadened X-ray peaks relative to STE. Software and computer hardware improvements helped further increase precision and accuracy in light element analysis of complex materials by offering more sophisticated procedures for the subtraction of continuum X-rays and including modern mass absorption coefficients. This advance led to better detection limits for materials where a simple calibration curve treatment is not appropriate, such as in the analysis of nitrogen in silicate glasses and minerals [1-4]. Over the last decade, another generation of LSM has become available for boron and carbon analysis (LDE6, Cr/C, 12 nm) as well as nitrogen analysis (LDE5, Cr/Sc, 8 nm), further improving sensitivity. However, a remaining problem for quantitative analysis arises from spectral peak shiffts and changes because the linear acquisition method with traditional wavelength dispersive (WDS) analysis makes acquiring the full peak spectrum time-prohibitive. Therefore, the recent availability of a new detector type for EPMA – the soft X-ray emission spectrometer (SXES, SXES-ER) by JEOL, Inc. – represents a very exciting addition to the mix of available analytical tools. The SXES is composed of a CCD area detector that can be coupled to multiple varied-line-spacing (VLS) aberration-corrected gratings (JS50XL, JS200N, JS300N, and JS2000) that cover a combined energy range from 50 eV to 2.3 keV. This provides higher spectral resolution and higher sensitivity for soft X-rays (< 1 keV) relative to traditional WDS spectrometers and allows simultaneous acquisition of the X-ray spectrum over the entire energy range of the grating (similar to energy dispersive analysis, EDS), and enables to perform hyperspectral mapping. Previous studies on boron, carbon, and nitrogen-bearing materials showed how SXES provides insight into electronic structure and bonding in materials [e.g., 5-8]. We used an SXES-ER with JS300N grating (83-830 eV) on a JEOL JXA-8530FPlus electron microprobe to explore its potential for X-ray spectroscopy and quantitative analysis, focusing on a range of minerals and glasses that contain high abundances of light elements and are relevant to the Earth Sciences. The EPMA instrument also has four traditional WDS spectrometers, which allows direct comparison of SXES and WDS-LSM spectra. A comparison of SXES and WDS-LSM spectra shows the much-improved spectral resolution for B, C and N using SXES (Figure 1). However, higher orders of more energetic X-ray lines are not suppressed using the SXES and can complicate spectral interpretation for quantitative analysis in complex materials. Figure 1 shows that the higher-order oxygen peaks partially interfere with both the Ka X-ray peak for boron in borosilicate glass (NIST SRMK326) and carbon in calcite (CaCO₃). On the other hand, the superior spectral resolution of the SXES brings back the potential for EPMA-based spectroscopy, as shown for a range of carbonate minerals (Figure 2), and introduces the ability of mapping for chemical states. We will discuss the advantages, challenges, and pitfalls of light element analysis by SXES and present examples of applications in the UMN lab. Overall,

SXES combined with electron microscopy provides a sensitive tool for elemental and chemical identification and spectroscopic exploration, especially for light elements.

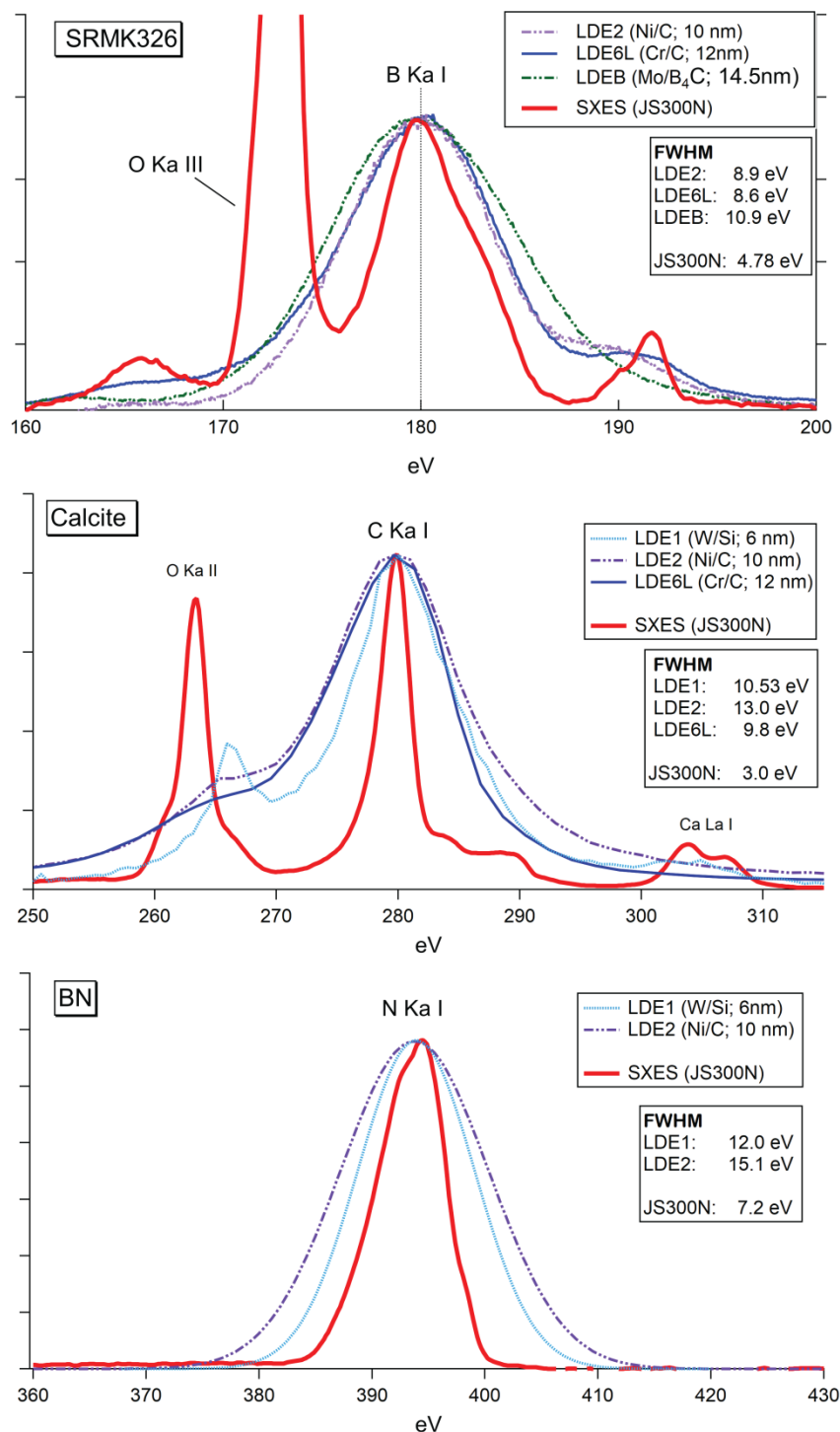


Figure 1. Figure 1. Comparison of peak shape widths of B, C and N between the SXES JS300N grating and WDS LSM's. Peak intensities are normalized to each other for better comparison of peak geometry.

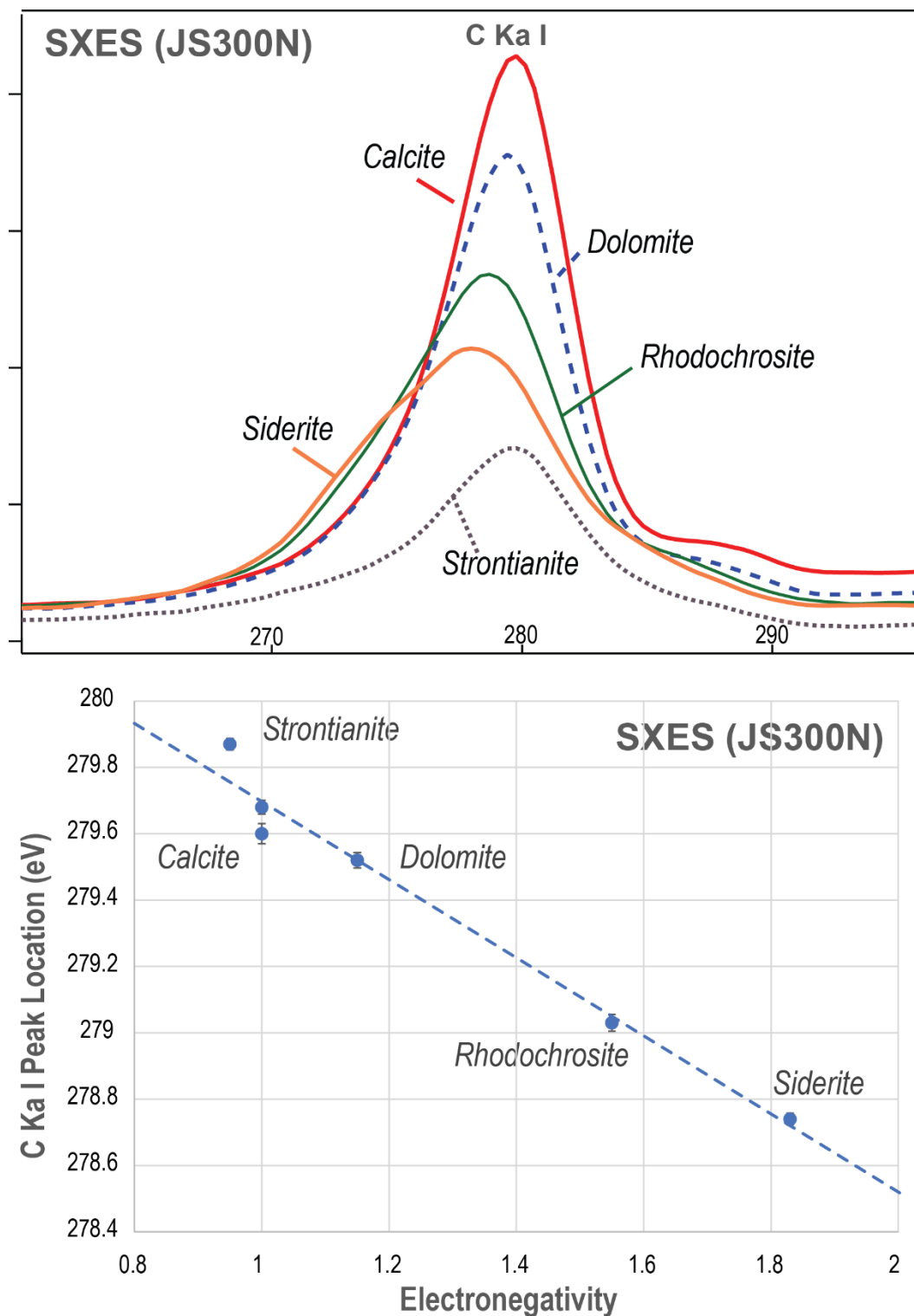


Figure 2. Figure 2: Comparison of C ka I peak shifts between different carbonate minerals analyzed with the JS300N grating at 10kV. The relative peak position compares well with the electronegativity of the dominant cation.

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