Investigation of N in Ammonium-bearing Silicates with Electron Probe Microanalysis (EPMA)

William Nachlas[1], Suzanne Baldwin[2], Jay Thomas[2] and Michael Ackerson[3]

[1]University of Wisconsin, Madison, Wisconsin, United States, [2]Syracuse University, Syracuse, New York, United States, [3]Smithsonian Institution, Washington, District of Columbia, United States

Nitrogen is a primary constituent of Earth's atmosphere and an essential component of many biological processes. Considerable effort has been dedicated to investigating N cycling in near-surface environments, and recent developments in understanding N incorporation into silicate minerals suggest that the solid earth and lithosphere could provide a substantial reservoir for the planetary N budget. Given the low diffusivity of N in some crustal silicates [1], it is possible that natural minerals exhibit fine-scale heterogeneity in their N contents. The quantity and distribution of this variation can retain a rich record of the kinetic and thermodynamic conditions of formation, and thus it is important to explore analytical methods capable of measuring low-level variations in N from µm-scale regions of solid materials.

Determining the concentration and distribution of low abundances of N in silicates presents a significant challenge in microanalysis. The primary analytical techniques capable of spatially-resolved investigation of N in solids are secondary ion mass spectrometry (SIMS), laser ablation mass spectrometry (LA-ICP-MS), and electron probe microanalysis (EPMA). While the former two methods are capable of better detection limits, they are limited to larger spot sizes, complicated by mass interferences, and require matrix-matched standard materials specific to each mineral system. We have tested capabilities for high spatial resolution quantification of low levels of N using EPMA.

There are several aspects of N quantification with EPMA that make it considerably more difficult than conventional measurements. Quantification of light elements ($N < 10$) is challenging because of low fluorescence yield, material-specific peak shape and position, strong absorption of light element x-rays by other components in the matrix, and spectral interferences from higher-order lines of heavier elements. Published attempts to determine N with EPMA endeavored to mitigate many of these challenges [2,3], and technological developments in instrumentation have substantially improved the capabilities for light element analysis, including the development of synthetic multilayered diffraction crystals and new spectrometer designs for improved resolution of low energy x-rays [4–6].

We investigated the concentration and distribution of N in a suite of ammonium-bearing silicate minerals that reflect the dominant N-bearing phases of the lithosphere: tobelite, buddingtonite, ammonioleucite, tsaregorodtsevite, and hyalophane. These minerals form during NH4-rich alteration of K-bearing silicate minerals, and the bonding environment of N in each mineral is likely to differ based on crystal structure. As a consequence, we observe that N peak shape and position differs between different samples (Fig. 1A). Given the low-energy distribution of N x-rays, there is potential for significant peak interferences in WDS spectra, especially with high-order x-ray lines emitted from transition row metals. Some of the studied minerals incorporate appreciable quantities of metallic species, and therefore it is necessary account for spectral interferences using overlap corrections and/or energy filtering. The overlap of Ti-Ll lines is particularly problematic for N determination given the similarity of x-ray energies (Fig. 1B), and we apply an off-peak overlap correction to account for this overlap in samples which contain significant Ti contents.

Our analysis routine involved quantification of N at 10 kV accelerating voltage and 20-100 nA beam current by aggregating N K-α counts on two synthetic multilayered diffraction crystals (PC1 and LPC0), followed by analysis of the remaining major and minor elements at 15 kV and 20 nA. An exponential background regression was applied to appropriately model background curvature in the vicinity of N lines, and time-dependent

intensity corrections were employed to mitigate N migration during prolonged irradiation of beam-sensitive materials. Quantitative WDS mapping of N performed at 5 kV and 400 nA reveal fine-scale heterogeneities in N concentration (Fig. 2). Using an optimized analytical routine for N quantification enables sensitivity approaching 0.02 weight% N and high-resolution quantitative mapping of sub-micron variations in N contents [7].
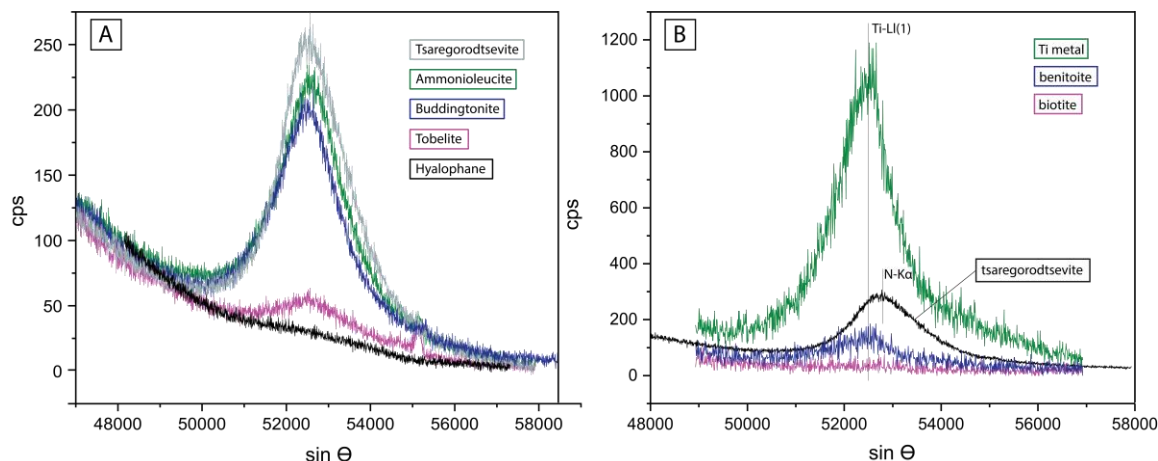
Figure 1. Figure 1. (A) Wavelength dispersive spectrometry scans using a PC1 diffraction crystal across the N position in our suite of ammonium-bearing silicate minerals reveals slight variations in peak shape and position between different samples. (B) Interferences on the N K-alpha position with high-order Ti-Ll lines must be accounted for using off-peak overlap corrections.
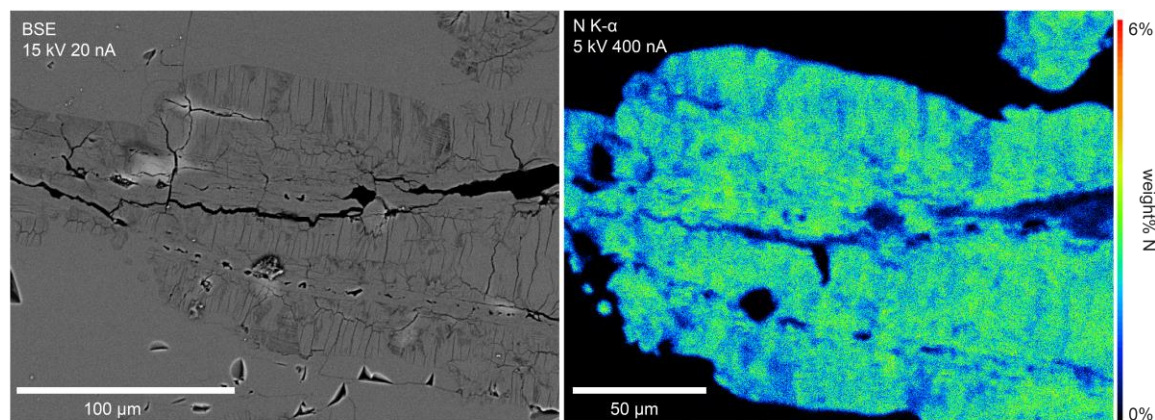
Figure 2. Figure 2. Backscattered electron imaging (A) and quantitative mapping of N (B) in a sample of ammonioleucite reveal fine-scale heterogeneities in N concentration.

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