

Analysis of ammonium in micas by Electron Energy-Loss Spectroscopy

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Since the late 1950's, ammonium has been recognized as an important interlayer constituent in white micas associated with organic matter. However, its identification has required special means that are not normally applied during routine analysis of low-grade metamorphic rocks. Indirect evidence of NH_4^+ comes from bulk chemical analysis and FTIR spectroscopy. However, the association of NH_4^+ with white mica cannot be unequivocally proven with these methods. X-ray powder diffraction can yield evidence of expanded 00l reflections, but the exact compositions of the ammonium bearing micas cannot be obtained with precision. Recent developments in electron energy-loss spectroscopy (EELS) has made it possible to directly locate and measure the compositions of NH_4^+ micas down to the nanometer scale. We have developed and tested methods for detecting N in micas also containing K. The method involves a simultaneous acquisition of EELS spectra over the energy-loss range 275-475 eV, using a dispersion of 0.2 eV, and the acquisition of energy dispersive X-ray spectra (EDS). The EELS spectra contain the core-loss edges for K $L_{2,3}$ (296.3 eV) and N K (400.9 eV). Thus, the N/K ratio can be calculated after background corrections. It is important to avoid areas containing carbon since the C K edge lies at 285 eV and interferes with simple extraction of K counts. When analyzing micas, the EDS analysis is used to calculate all other elements and a mineral formula based on 6 tetrahedral and octahedral cations is generated. The absolute ammonium content is then calculated by combining the two analyses.

The validity of EELS analysis was tested by analyzing potassium nitrate. Correct answers were derived from analyses that were obtained in the first few seconds of beam exposure, since potassium nitrate underwent progressive damage and mass loss during analysis. The N K near-edge structure also evolved with time indicating a change in bonding and or structural of N with time. On the other hand, extended exposure of ammonium micas did not indicate a change in the value of N/K over time with analyses using a defocused beam.

Results of the application to tobelitic white micas coexisting with muscovite confirm the compositional gap hypothesized by Nieto (2002). Analyses of ammonium in white micas from the Central Alps (Switzerland) indicate that concentrations of N down to 0.01 atoms per formula unit (based on 11 oxygens) can be detected. Application of this method to coexisting muscovite and paragonite from the Carpathian Mountains shows that NH_4^+ is preferentially partitioned into muscovite. This technique promises to reveal far more compositional detail in white micas associated with maturing organic matter than previously possible.

References

Nieto, F. (2002). *Am. Mineral.*, 87, 205-216.