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Experimental quantification of the Fe-valence state at amosite-asbestos boundaries using acSTEM dual-electron energy-loss spectroscopy

Ruggero Vigliaturo[1,*], Simone Pollastri[2], Reto Gieré[1,3], Alessandro F. Gualtieri[4], and Goran Dražić[5]

[1]Department of Earth and Environmental Science, University of Pennsylvania, 240 South 33rd Street, Hayden Hall, Philadelphia, Pennsylvania 19104-6316, U.S.A. Orcid 0000-0001-6957-5396
[2]CERIC–ERIC, Strada Statale 14-km 163.5, 34149 Basovizza, Trieste, Italy
[3]Center of Excellence in Environmental Toxicology, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6316, U.S.A.
[4]Dipartimento di Scienze Chimiche e Geologiche, Università degli studi di Modena e Reggio Emilia, I-41125, Modena, Italy
[5]Department for Materials Chemistry, National Institute of Chemistry, Hajdrihova ulica 19, 1000, Ljubljana, Slovenia

Abstract

Determination of the oxidation state and coordination geometry of iron in Fe-bearing minerals expands our knowledge obtained by standard mineralogical characterization. It provides information that is crucial in assessing the potential of minerals to interact with their surrounding environment and to generate reactive oxygen species, which can disrupt the normal function of living organisms. Aberration-corrected scanning transmission electron microscopy dual-electron energy-loss spectroscopy (acSTEM Dual-EELS) has only rarely been applied in environmental and medical mineralogy, but it can yield data that are essential for the description of near-surface and surface mechanisms involved in many environmental and health-related processes. In this study, we have applied the energy loss near-edge structure (ELNES) and $L_{2,3}$ white-line intensity-ratio methods using both the universal curve and progressively larger integrating windows to verify their effectiveness in satisfactorily describing the valence state of iron at amosite grain boundaries, and, at the same time, to estimate thickness in the same region of interest. The average valence state obtained from acSTEM Dual-EELS and from a simplified geometrical model were in good agreement, and within the range defined by the bulk and the measured surface-valence states. In the specific case presented here, the use of the universal curve was most suitable in defining the valence state of iron at amosite grain boundaries. The study of ELNES revealed an excellent correspondence with the valence state determined by the $L_{2,3}$ white-line intensity-ratio method through the use of the universal curve, and it seems that the spectra carry some information regarding the coordination geometry of Fe. The combination of visual examination, reconstruction of the grain boundaries through a simple geometrical model, and Dual-EELS investigation is a powerful tool for characterizing the grain boundaries of hazardous minerals and foreseeing their potential activity in an organism, with the possibility to describe toxic mechanisms in a stepwise fashion.

Keywords: Dual electron energy loss spectroscopy, Fe-valence state, amphibole, asbestos, surface chemistry, spatially resolved crystal chemistry