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

RUGGERO VIGLIATURO1*, SIMONE POLLASTRI2, RETO GIERÉ1,3, ALESSANDRO F. GUALTIERI4, AND GORAN DRAŽIĆ5

1Department 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
2CERIC–ERIC, Strada Statale 14-km 163.5, 34149 Basovizza, Trieste, Italy
3Center of Excellence in Environmental Toxicology, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6316, U.S.A.
4Dipartimento di Scienze Chimiche e Geologiche, Università degli studi di Modena e Reggio Emilia, I-41125, Modena, Italy
5Department 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 L2,3 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 L2,3 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

INTRODUCTION

The valence state of Fe in members of the amphibole supergroup plays an important role when elucidating mineralogical and geological history since it can be influenced by multiple geochemical reactions under a wide range of conditions (Cavé et al. 2006). It can further contribute to the understanding of the redox conditions in which these minerals crystallized (Garvie and Busek 1998) and of weathering, dissolution, and recrystallization processes to which these minerals were exposed in the natural environment. When in contact with living cells, the mixed-valence state of Fe in amphiboles can determine the mineral’s potential in disrupting Fe homeostasis and in generating reactive oxygen species (ROS) in cells and at the systemic level (Jablonski et al. 2017). The generation of ROS may lead to several respiratory diseases (e.g., asbestosis, pleural abnormalities) and malignancies, such as squamous cell carcinoma, small-cell and large-cell carcinoma, and adenocarcinoma (Pacella et al. 2012), including mesothelioma, which is strictly related to asbestos minerals. Amphiboles that are not necessarily classified as asbestos or asbestiform were recently also suggested to be related to autoimmune disease (Li et al. 2012; Ferro et al. 2013; Pfau et al. 2014), which makes the description of the toxicity caused by these minerals even more pressing. During interaction with the biological environment, Fe in asbestiform minerals plays different roles depending on its oxidation state, coordination, and surface-site occupancy (Gualtieri et al. 2016). ROS may be generated when Fe is released into cells or biofluids or during surface-bound Fe-promoted reactions (Schoonen et al. 2006). Therefore, the possibility to determine both valence and bonding of Fe at an atomic- or nano-scale allows for a detailed description of the mechanisms that can potentially lead to