Analysis of erionites from volcaniclastic sedimentary rocks and possible implications for toxicological research

MARTIN HARPER1,*, ALAN DOZIER2, JULIE CHOУINARD3, AND ROBYN RAY4

1Exposure Assessment Branch, Health Effects Laboratory Division, National Institute for Occupational Safety and Health, 1095 Willowdale Road, MS-3030, Morgantown, West Virginia 26505, U.S.A.
2Chemical Exposure & Monitoring Branch, Division of Applied Research & Technology, National Institute for Occupational Safety & Health, 1090 Tusculum Avenue, MS-R7, Cincinnati, Ohio 45226, U.S.A.
3Center for Advanced Materials Characterization in Oregon (CAMCOR), University of Oregon, 1443 E. 13th Avenue, Eugene, Oregon 97403, U.S.A.
4EMSL Analytical, Inc., 200 Route 130 North, Cinnaminson, New Jersey 08077, U.S.A.

ABSTRACT

Erionite occurs in volcaniclastic rocks and soils; in some villages in Turkey the presence of erionite in local rocks is associated with mesothelioma, a disease also associated with inhalation of airborne asbestos. Since volcaniclastic rocks containing erionite are widely present in the western U.S.A., there is a concern over potential health issues following inhalation of dust particles in these areas and thus there is a need to identify and quantify erionite particles found in air samples during hygienic investigations. Previous attempts to analyze the few micrometer-sized erionite particles found on air sample filters under transmission electron microscope (TEM) encountered difficulties due to electron beam damage. Recommendations are presented for accurate analysis by both energy-dispersive spectroscopy (EDS) and selected-area electron diffraction (SAED). Much of the work previously published to establish the crystal chemistry of erionite has involved the relatively large crystals found in vesicles of extrusive volcanic rocks. Analysis of these crystals gives a weight percent ratio of Si to Al in a narrow range around 2.7 (molar ratio 2.6), consistent with a unit-cell formula Al10Si26. In addition, the cation contents of these crystals generally meet the charge balance error formula for zeolites. However, erionites formed in volcaniclastic sedimentary rocks (tuffs) have very different Si:Al weight percent ratios, around 4.0, which is above the upper range for the analyses of the crystals found in vesicles. Analysis of many particles in samples from different locations reveal two other major differences between the erionites from the sedimentary situations and those found in vesicles. (1) The extra-framework cation (Na, K, Ca) contents are lower than required for a stoichiometric balance with framework Al substitution for Si so that the cation charge balance error formula limits for zeolites are not met. (2) There is a large variability in measured cation contents from particle to particle from the same source as well as substantial differences in average compositions from different sources. However, sedimentary erionites cannot be termed a separate mineral species because the crystallographic data are consistent with erionite and new zeolite names cannot be proposed on the basis of Si:Al ratios alone. In addition to chemical differences between erionite from different sources, there are also morphological differences. By analogy with asbestos minerals, differences in composition and morphology may have implications for relative toxicity, and future research should include consideration of these aspects.

Keywords: Analysis, chemical (mineral), erionite, electron microscopy, medical mineralogy, zeolites

INTRODUCTION

Erionite is a naturally occurring mineral that belongs to a group of silicate minerals called zeolites. It was originally described from the Durkee opal mine near Durkee, Baker County, Oregon, and named by Eakle (1898). The name was derived from a Greek word that means wool because at the type locality the erionite occurs as white, wool-like fibers. However, this is an uncommon habit, which has also been observed in the Reese River zeolite deposits, near Austin, Nevada (Gude and Sheppard 1981), but not elsewhere. For more than half a century, this zeolite was considered extremely rare, and no additional occurrences were listed until Deffeyes (1959) described material from Nevada and Wyoming. Unlike the type erionite, these subsequent occurrences were either crystals formed in the vesicles of (mainly) basaltic lavas, or microscopic acicular-to-fibrous crystals in diagenetically altered, silicic, vitric tuffs of Cenozoic lacustrine deposits (Mumpton and Ormsby 1976). In most cases the erionite is likely to be a later, pore-filling, re-crystallization of dissolved volcanic glass. Numerous additional discoveries of erionite have been reported throughout the world, for example

* Present address: Zefon International, Inc., 5350 SW 1st Ln, Ocala, FL 34744, U.S.A. E-mail: mharper@zefon.com