Environmental applications of the LANL nuclear microprobe

D.D. Hickmott [a,*], J.M. Herrin [a], R. Abell [a], M. George [a], J. Stimac [b],
E.R. Gauerke [c], R.F. Denniston [c]

[a] Los Alamos National Laboratory, EES-1, MS-D462, Los Alamos, NM 87545, USA
[b] Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada
[c] Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA

Abstract

The LANL nuclear microprobe has been used to study the distributions of trace elements (TE) of environmental interest including: (1) metals in coal and fly ash, (2) Pb in the Bandelier Tuff (BT), (3) Ba in tree rings, (4) Mn, Fe, Sr and Y in Yucca Mountain calcites. These studies illustrate environmental problems that can be addressed using nuclear microprobes. Micro-PIXE (MP) analyses with 5–10 micrometer spatial resolution provide constraints on processes that redistribute contaminants in the environment, and hence may help answer environmental problems where fine-scale chemical records are important. MP analyses of particulates in coal and ash show that pyrite contains As, Se, Hg and Pb; macerals contain Cr, halogens and S; cenospheres contain As, Se and Ni; and hematite ash contains Ni and As. Understanding these elemental modes of occurrence allows prediction of metal behavior in boilers and may enhance compliance with the Clean Air Act Amendments. Fine-grained high-Pb minerals were identified using SEM and MP analyses of BT minerals. These minerals were from samples associated with deep-groundwater wells containing Pb at levels greater than regulatory limits. Pb is concentrated in Pb minerals (e.g. cerussite), smectite, and hematite formed during low-T alteration of tuff. Understanding mineralogic speciation of metals may provide insights into sources of groundwater pollution. Tree rings from ponderosa pines that grew in a Ba-contaminated drainage were analyzed using MP. Ba concentrations are typically higher in rings that formed after operations discharging Ba to the environment began. Such tree-ring analyses may ultimately provide information on rates of contaminant migration in the environment. TE in zoned calcites from Yucca Mountain were analyzed by MP. Calcites from the saturated zone (SZ) have distinct chemical signatures (high Fe, Mn and low Y). No calcites in the unsaturated zone with SZ chemical signatures were found using MP. MP analyses of vein minerals can provide insights into mineral sources and hydrogeologic processes. These examples show that TE microanalysis with nuclear microprobes can provide insights into a wide variety of environmental processes. Such information allows more informed, technically defensible negotiations with regulators, saving time and money in environmental cleanup projects. © 1997 Elsevier Science B.V.

1. Introduction

Environmental issues represent a significant area of concern in the United States and world-wide.

Metal contaminants, particularly Pb, Hg, As and Cr, are present at a significant fraction of contaminated sites slated for characterization under the United States' Superfund program. They represent a significant problem to the mining, coal and utility, and defense/nuclear industries world-wide.

Macro-proton Induced X-ray Emission analysis

* Corresponding author. Fax: + 1-505-665-3285;
email: dhickmott@lanl.gov

(PIXE) has been used to investigate environmental problems since widespread utilization of PIXE began during the 1970s [1]. Notable applications of macro-PIXE to environmental problems include: (1) studies of aerosols and particulates in support of studies of air quality and global climate change, (2) analyses of bulk environmental samples, such as waters, and (3) studies of biological materials such as tree rings [2–4]. These studies typically take advantage of the low detection limits, small sample volumes, and broad range of element sensitivity that PIXE is capable of providing — particularly when compared with competing analytical methods. Comprehensive reviews of macro-PIXE applications to environmental problems include papers by Malmqvist [5], and Ghermandi and co-workers [6].

During the past decade micro-PIXE has also been used to investigate environmental problems. Reviews of applications of micro-PIXE to environmental issues have also appeared recently. Those of Grime and Watt [7], Malmqvist [8,9] and Orlić [10] provide coverage of the literature through approximately 1995.

This paper outlines recent Los Alamos National Laboratory (LANL) applications of micro-PIXE to environmental problems. It also reviews applications of nuclear microprobes to environmental problems that have appeared during the past two years. The LANL nuclear microprobe has been used to investigate two main classes of environmental problems — examination of metal speciation in contaminated environmental media, and sequential analyses of materials that provide time-series insights into environmental contamination. These applications take advantage of the unique capabilities of PIXE microanalysis compared to the majority of other environmental analytical methods, including macro-PIXE. Applications in fields closely related to environmental sciences, such as biology, toxicology, and animal physiology will not be addressed in this review, because they are being reviewed in other articles for these proceedings.

2. Analytical

Analyses were made using the LANL nuclear microprobe, which is located in the Ion Beam Mate-rials Laboratory. Operation and data reduction procedures for the LANL microprobe are described in detail by Duffy et al. [11] Rogers et al. [12,13] and Burnett et al. [14] and are summarized below. All of these studies used a 3 MeV proton beam focused to a 5–20 μm diameter spot.

The LANL microprobe differs from most other nuclear microprobes because it uses a superconducting solenoid, rather than a quadrupole lens, as the final focusing system. Advantages of this lens include high beam-current densities, which reduce count times. Disadvantages include a lack of scanning capability and potential sample damage due to high beam-current densities. Typical beam currents were 1–10 nA and data acquisition times were typically 5–15 min. A 170 eV resolution SiLi detector was used to collect X-ray spectra. Combinations of Be (58.231 mg/cm^2) and Al (13.117 to 80.675 mg/cm^2) filters attenuated major-element X-rays and minimized analytical deadtimes.

Quantitative analyses were obtained using the constrained least-squares data reduction method of Duffy et al. [11]. This technique uses major-element analyses of each PIXE point, typically obtained by electron microprobe analysis, to calculate the relative intensities of K, L and M X-rays for each element in a sample matrix prior to spectrum fitting, and normalizes the PIXE spectrum to the concentration of a major element. Note that in the tree-ring study described below that current-normalized counts, rather than concentrations, are reported because no major element measurable by electron microprobe analysis was present in the rings. The fitting procedure takes sample geometry, major-element absorption edges, and filter thicknesses into account, but ignores low-energy tails of X-ray peaks and secondary X-ray fluorescence. For most of the materials described in these studies, these problems are minor.

The LANL PIXE data reduction method typically yields data that are accurate within counting statistics of accepted values for geologic standards analyzed by other methods [13–16]. Significant sources of error in quantitative analyses of environmental samples include: (1) overlap of multiple phase grains by the impinging proton beam, (2) inaccuracies in the determination of the normalizing major element, and (3) volatilization of light elements by thermal damage in the proton beam. The first of these problems

is probably the most serious. Environmental phases are often fine-grained, so mixed analyses are a major problem. The most effective method to monitor this problem is to examine multiple analyses of a phase in a sample for anomalous elemental concentrations. In cases where such anomalous concentrations were significant in the studies described below, the suspect analyses were discarded. Volatilization is most significant for light elements such as sulfur. The heavy metals that represent the principal focus of these case studies are less susceptible to volatilization.
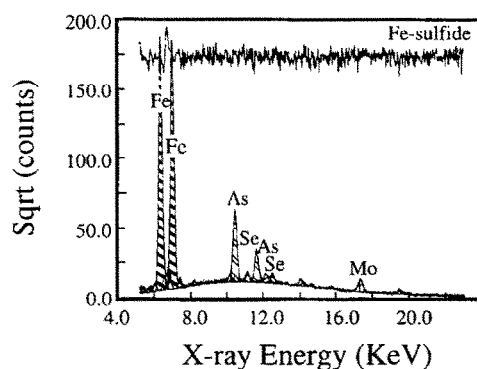

Fig. 1. PIXE spectrum of sulfide grain from lower-Kittanning coal. Note high concentrations of As, Se and Mo. Residuals to least-squares fit shown at top of spectrum. After Ref. [27].

3. Toxic-metal speciation in environmental media

Mineralogic speciation of metals in environmental media determines: (1) the solubility of the metal in environmental fluids, (2) the bioavailability of the metal to environmental receptors, and (3) the long-term stability and dispersion mechanisms of the metal in the environment. Speciation studies that have been completed using micro-PIXE analyses of environmental media include investigations of (1) individual aerosol particles [8,17–26], (2) lake sediment particles and pore-waters [7], and (3) environmental weathering products [7].

3.1. Toxic metal speciation in coal and coal ash

The Clean Air Act Amendments of 1990 stipulate that 11 toxic metals found in coal require further study to determine potential risks to receptors due to dispersal of these metals by utility-fired boilers. Metal speciation and abundances in coals and flyash determine the amounts of toxic metals that are emitted via coal-fired power plant stacks.

The LANL nuclear microprobe has been used to study metal speciation in the lower Kittanning coal of Pennsylvania [27], in western United States coals [28], and in ash collected at a small-scale combustor. Significant results of these studies include: (1) identification of strong partitioning of As, Se, and Mo into coal sulfides (Fig. 1) and Cr and halogens into coal macerals, (2) identification of trace-element signatures in coal sulfides that may be due to influences of marine fluids, and (3) determination of partitioning of As, Se and Ni into cenospheres and Ni and As

into hematite ash in bottom ash and flyash. Ultimately, information on metal speciation in fossil fuels and combustion by-products may be used as input into computer codes that simulate combustion processes.

3.2. Lead mineralogic speciation in the Bandelier Tuff, Los Alamos, NM

Recent analyses of samples from deep groundwater in the southwest portions of LANL have shown levels of Pb above Environmental Protection Agency regulatory limits [29]. Although low, these levels are of concern because Pb was used in large quantities in hydrodynamic tests at a LANL site in which high-Pb well waters were obtained. These tests also included dozens of kilograms of plutonium and enriched uranium, each in subcritical quantities.

Lead mineralogic speciation in rocks and soils determines the concentrations of that element in associated surface and groundwaters. Micro-PIXE, scanning electron microscopy (SEM), and electron microprobe analysis were used to determine the mineralogic speciation of Pb in the Bandelier Tuff, the rock unit in which the anomalously high Pb concentrations in water were found [30]. Micro-PIXE analyses revealed that significant amounts of Pb were concentrated in primary igneous phases such as volcanic glass, and in alteration minerals such as hematite and smectite (Fig. 2). SEM investigations revealed vapor phase minerals such as galena, cerussite, Pb-selenide, and pyromorphite. Micro-PIXE and
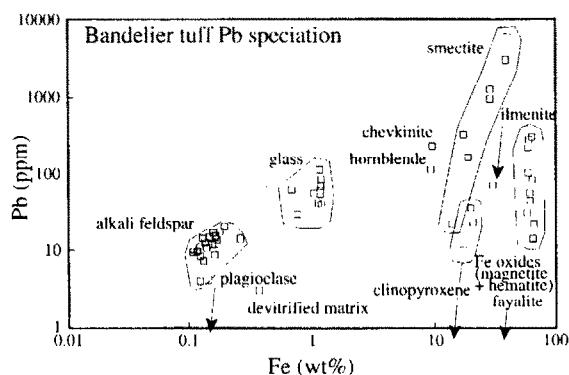
Fig. 2. Fe concentration versus Pb concentration for minerals from the Bandelier tuff as determined by micro-PIXE and electron-microprobe analysis. Note high concentrations in hydrothermal/ vapor phase minerals smectite and hematite. After Ref. [30].

SEM analyses showed that secondary minerals produced during vapor-phase alteration were a likely source for high-Pb abundances in groundwaters [30]. Solubility/partitioning calculations show that the Pb concentrations found in groundwater are fully compatible with the observed Pb-mineral bearing assemblage. Micro-PIXE analyses of Pb mineralogic speciation are an important component in negotiations with regulatory agencies regarding environmental-contamination pathways.

4. Tracing environmental processes

If a mineral or organic particle grows during a change in the physicochemical parameters affecting the particle, the change will be manifest by variation in the chemical composition of particulates. Tree rings and foliage [9,31–33], ostracod or bivalve shells [34–36], multiple generations of vein minerals, and tooth enamel [37,38] are all examples of environmentally-significant materials that have been investigated by micro-PIXE that can reflect changes in composition of fluids and changes in other physicochemical parameters during particulate growth. Such studies are of importance in environmental investigations because they may provide insights: (1) into contaminant variability over time due to changes in concentrations of an element in the environment, (2) into temperature variations over time due to climate change or other factors, and (3) into degree of metal

incorporation into environmental receptors as a result of seasonal fluctuations.

4.1. Barium in tree rings at LANL

The rate of mobility of inorganic constituents in the environment near contaminated sites is an important factor in environmental decision making. Risk assessments require an understanding of concentrations of environmental pollutants both in the present and in the future. In theory, variations in element abundance in tree rings and other growth-zoned biological materials should indicate when a surface contaminant plume impacts a location downgradient from a contaminated area. In a preliminary study, relative abundances of Ba in tree rings downgradient from a contaminated site at LANL were investigated to determine the feasibility of using micro-PIXE tree-ring studies for tracking heavy metals in the environment.

Barium nitrate was a major component of explosive systems in early United States' nuclear weapons. Several sites at LANL contain Ba in soils at levels up to 30 000 ppm. These levels present a potential risk to human health and the environment.

The LANL nuclear microprobe was used to determine relative variations in Ba in rings in a ponderosa pine directly downgradient from the most highly Ba-contaminated site at LANL. Absolute concentrations of Ba could not be determined using the LANL data reduction software, because no major elements were present in the tree-rings at levels that could be analyzed quantitatively using electron-microprobe analysis. Thus, relative variations in Ba abundance, as reflected by Ba counts normalized to constant charge, were used as a proxy for Ba concentrations. Fig. 3 shows a PIXE spectrum of a tree ring from 1979.

Barium abundance, as measured by changes in total counts within Ba K X-ray peaks, range from 130 counts in 1941, 220 counts in 1957, > 350 counts in 1958, and 300 counts in 1979 (Fig. 4). Two other trees downgradient from the contaminated site exhibit grossly similar Ba variations. This variability reflects the initiation of Ba-waste-producing operations at this site in 1951, and the decrease in Ba use in the 1960s and 1970s. In addition, the original form of Ba, Ba nitrate, is converted into insoluble Ba
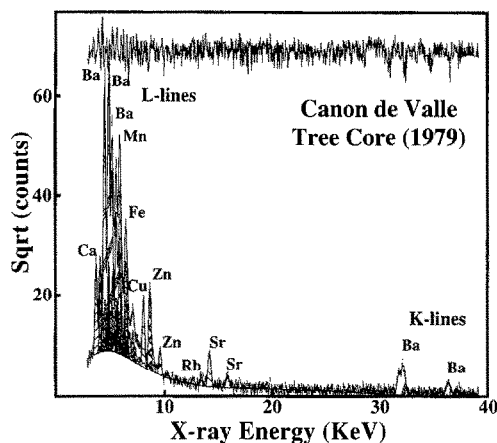
XI. ENVIRONMENTAL SCIENCE

Fig. 3. PIXE spectrum of tree ring dated as forming in 1979. Note K and L X-ray peaks for Ba, which is a contaminant at many sites at LANL. Residuals to least-squares fits shown at top of spectrum.

4.2. Trace elements in Yucca Mountain calcites

Yucca Mountain, Nevada, is being studied as a potential repository for United States' high-level nuclear waste. Geologic and geochemical studies of Yucca Mountain focus on understanding the long-term stability of the proposed repository, which would be located within unsaturated tuffaceous volcanic rocks. Calcite is a minor but widely distributed mineral at Yucca Mountain, both in the unsaturated and saturated zones [39,40]. Calcite deposits are particularly important to geochemical studies of the environmental stability of Yucca Mountain because: (1) calcite is one of the youngest minerals found at Yucca Mountain; (2) calcite deposits indicate locations and provide constraints on timing of fluid flow and minerals' precipitation; (3) studies of calcite chemistry can provide clues concerning the chemistry of fluids that have transported elements (strontium and the lanthanides) that are of concern in high-level nuclear wastes. Isotopic and trace-element studies of calcite mineral separates [41–43] suggest that unsaturated-zone and shallow saturated-zone calcites are derived from pedogenic sources, and deep saturated-zone calcites precipitated from compositionally-distinct deep fluid sources.

Microanalytical studies, which use electron microprobe analysis, Secondary Ion Mass Spectrometry (SIMS) [44], or micro-PIXE, provide constraints on fluid flow at Yucca Mountain. Fine-scale trace-element abundance resolution can show whether small-scale incursions of fluids similar to those that precipitated the deep-saturated zone calcites have deposited materials in the unsaturated zone.

Preliminary micro-PIXE analyses of calcite from three samples from Yucca Mountain, two from the unsaturated zone and one from the deep-saturated zone suggest: (1) that saturated zone calcites have higher manganese and iron and generally lower yttrium than unsaturated zone calcites (Fig. 5) [45]; and (2) that fine-scale growth zones, observed in cathodoluminescence studies in calcite from unsaturated intervals, do not appear to have precipitated from fluids similar to saturated-zone fluids. Micro-PIXE analyses were sited on zones of varying cathodoluminescence activity to investigate the fine-scale variation in calcite chemistry in the unsaturated and saturated zones. More extensive SIMS studies of

carbonate (witherite) and Ba sulfate (barite) during exposure to the environment. These Ba compounds are less soluble than Ba nitrate and thus are probably less bioavailable to plants than Ba nitrate.

Although this study is preliminary, it suggests that micro-PIXE investigations of tree rings and other biological materials can be used to measure the progress of heavy metals through the environment. Further studies of (1) radial variations in element concentatration in individual trees, (2) the effects of variation in climate, metal speciation, and soil type on Ba incorporation into plant materials, and (3) translocation of Ba and other metals between tree rings following growth are required prior to establishment of this technique for environmental pollution monitoring.
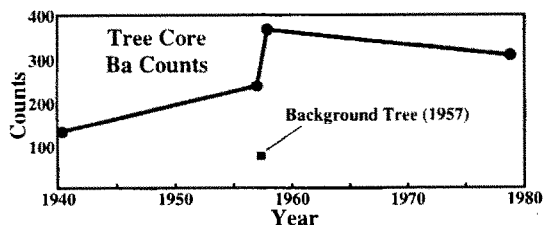

Fig. 4. Ba abundance (total counts within Ba K X-ray peaks) versus year of growth for tree rings from ponderosa pine downgradient from a highly Ba-contaminated LANL site.
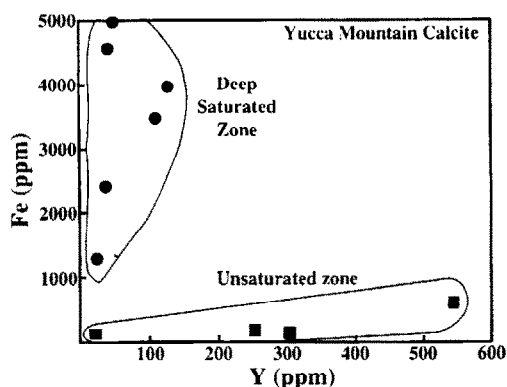
Fig. 5. Fe concentration versus Y concentration for Yucca Mountain calcites as determined by micro-PIXE. Unsaturated zone calcites = circles, saturated zone calcites = squares.

Yucca Mountain calcites support these preliminary micro-PIXE results [44].

This study illustrates that trace-element microanalytical methods such as PIXE and SIMS can illuminate fine-scale variations in fluid flow in vadose zones. If different fluid sources have distinct trace-element chemistries, then fluid-flow directions and magnitudes can be inferred from trace-element studies of zoned vein minerals such as calcite. Such studies are important for performance assessments at sites such as Yucca Mountain, for sites regulated under Superfund or RCRA, and for waste-disposal sites such as LANL's radioactive waste disposal site — Area G.

5. Conclusions

Nuclear microprobe and other trace-element microanalytical techniques can help solve environmental problems. The two principle classes of problem that can be addressed using nuclear-microprobe techniques are tracking the rate and mechanism of contaminant migration in the environment and determining the mineralogic speciation of contaminants in the environment. Both of these types of information provide important science-based tools in negotiations with environmental regulators. Micro-PIXE is a mature analytical method that should be able to be used in regulatory negotiations concerning environmental problems.

Challenges to nuclear microprobe operators in coming years include (1) development of accurate methods of quantifying analyses of very fine-grained (< 1 μm) particles; (2) improvement of automated particle analysis methods in order to acquire statistically-significant numbers of particle analyses rapidly and accurately; and (3) ensuring acceptance of nuclear microprobe-generated data by environmental regulators. In order to achieve such goals it will be necessary to develop common analysis methods and standards that can be used in multiple laboratories to ensure the quality and reproducibility of micro-PIXE results that may be used in environmental decision making.

Acknowledgements

References

[1] J.A. Cooper, Nucl. Instr. and Meth. 106 (1973) 525.
[2] G.S. Hall, Nucl. Instr. and Meth. B49 (1990) 60.
[3] K. Pernestal, H.K. Li, Nucl. Instr. and Meth. B 49 (1990) 261.
[4] G.A. Glass, K.H. Hasenstein, H.T. Chang, Nucl. Instr. and Meth. B 79 (1993) 393.
[5] K.G. Malmqvist, Nucl. Instr. and Meth. B 231 (1984) 529.
[6] C. Ghermandi, R. Cecchi, P. Laj, Nucl. Instr. and Meth. B 109 (1996) 63.
[7] G.W. Grime, F. Watt, Nucl. Instr. and Meth. B 75 (1993) 495.
[8] K.G. Malmqvist, Nucl. Instr. and Meth. B 85 (1994) 84.
[9] K.G. Malmqvist, Nucl. Instr. and Meth. B 113 (1996) 336.
[10] I. Orlić, Nucl. Instr. and Meth. B 104 (1995) 602.
[11] C.J. Duffy, P.S.Z. Rogers, T.M. Benjamin, Nucl. Instr. and Meth. B 22 (1987) 91.
[12] P.S.Z. Rogers, C.J. Duffy, T.M. Benjamin, C.J. Maggiore, Nucl. Instr. and Meth. 231 (1984) 671.
[13] P.S.Z. Rogers, C.J. Duffy, T.M. Benjamin, Nucl. Instr. and Meth. B 22 (1987) 133.
[14] D.S. Burnett, D.S. Woolum, T.M. Benjamin, P.S.Z. Rogers, C.J. Duffy, C.J. Maggiore, Geochim. Cosmochim. Acta 53 (1989) 471.

[15] J. Stimac, D.D. Hickmott, Chem. Geol. 117 (1994) 313.

[16] D.D. Hickmott, B.E. Treves, G.T. Roselle and L.P. Baumgartner, these proceedings (ICNMTA-96), Nucl. Instr. and Meth. B 130 (1997) 660.

[17] H.R. Wilde, W. Bischof, B. Raith, C.D. Uhlhorn, B. Gonsior, Nucl. Instr. and Meth. 181 (1981) 165.

[18] M. Jaksic, F. Watt, G.W. Grime, E. Cereda, G.M.B. Marcazzan, V. Valkovic, Nucl. Instr. and Meth. B 56–57 (1991) 699.

[19] E. Cereda, M. G.M.B., M. Pedretti, G.W. Grime and A. Baldacci, Atmos. Environ. 29 (1995) 2323.

[20] E. Cereda, G.M. Braga Marcazzan, M. Pedretti, G.W. Grime, A. Baldacci, Nucl. Instr. and Meth. B 104 (1995) 625.

[21] I. Orlić, T. Osipowicz, F. Watt, S.M. Tang, Nucl. Instr. and Meth. B 104 (1995) 630.

[22] E. Cereda, G.M.B. Marcazzan, G.W. Grime, F. Mattachini, Nucl. Instr. and Meth. B 109 (1996) 696.

[23] E. Cereda, G.M.B. Marcazzan, M. Pedretti, G.W. Grime, A. Baldacci, J. Aerosol Sci. 27 (1996) 607.

[24] W. Jambers, R. Vangrieken, Trends Anal. Chem. 15 (1996) 114.

[25] W. Jambers, L. Debock, R. Vangrieken, Fresenius J. Anal. Chem. 355 (1996) 521.

[26] W. Maenhaut, R. Salomonovic, J. Ptasinski and G.W. Grime, these proceedings (ICNMTA-96), Nucl. Instr. and Meth. B 130 (1997) 576.

[27] D.D. Hickmott, W.S. Baldridge, Econ. Geol. 90 (1995) 246.

[28] D.D. Hickmott, presented at 7th Int. Conf. on Coal Science, Banff, Alberta, Canada (1993).

[29] W.D. Blake, F. Goff, A.I. Adams and D. Counce, Los Alamos National Laboratory Report, Los Alamos, New Mexico LA- 12912 (May 1995).

[30] J. Stimac, D.D. Hickmott, R. Abell, A. Larocque, D. Broxton, J. Gardner, S. Chipera, J. Wolff and E. Gauerke, J. Volcanol. Geotherm. Res., in press.

[31] N.E.G. Lovestam, E.M. Johansson and J. Pallon, Nucl. Instr. and Meth. B 49 (1990) 490.

[32] Z.Q. Lin, P.H. Shuepp, Environ. Sci. Technol. 30 (1996) 246.

[33] W.J. Przybyłowicz, C.A. Pineda, V.M. Prozesky, J. Mesjasz-Przybyłowicz, Nucl. Instr. and Meth. B 104 (1995) 176.

[34] G.E. Coote, W.J. Trompetter, Nucl. Instr. and Meth. B 77 (1993) 501.

[35] J. Nystrom, U. Lindh, E. Dunca, H. Mutvei, Nucl. Instr. and Meth. B 104 (1995) 612.

[36] Z. Dai, C. Ren, Q. Zhao, P. Wang, F. Yang, Nucl. Instr. and Meth. B 104 (1995) 619.

[37] G.E. Coote, T.W. Cutress and G. Suckling, Nucl. Instr. and Meth. B, this volume.

[38] T.W. Cutress, G.E. Coote, M. Shu, E.I.F. Pearce, Caries Res. 30 (1996) 204.

[39] D.T. Vaniman, Los Alamos National Laboratory Report, Los Alamos New Mexico LA 12720-MS (April 1994).

[40] D.T. Vaniman, S.J. Chipera, D.L. Bish, Geoderma 63 (1994) 1.

[41] Z.E. Peterman, J.S. Stuckless, B.D. Marshall, S.A. Mahan and K. Futa, Proc. 3rd Int. Conf. on High Level Radioactive Waste Management (1992) p. 1582.

[42] J.F. Whelan and J.S. Stuckless, Proc. 3rd Int. Conf. on High Level Radioactive Waste Management (1992) p. 1572.

[43] D.T. Vaniman and S.J. Chipera, Geochim. Cosmochim. Acta, submitted.

[44] R.F. Denniston, M.S. Thesis, University of New Mexico, Albuquerque, NM (1995).

[45] R.F. Denniston, E.R. Gauerke, C.K. Shearer, D.T. Vaniman, D. Hickmott, EOS 74 (1993) 677.