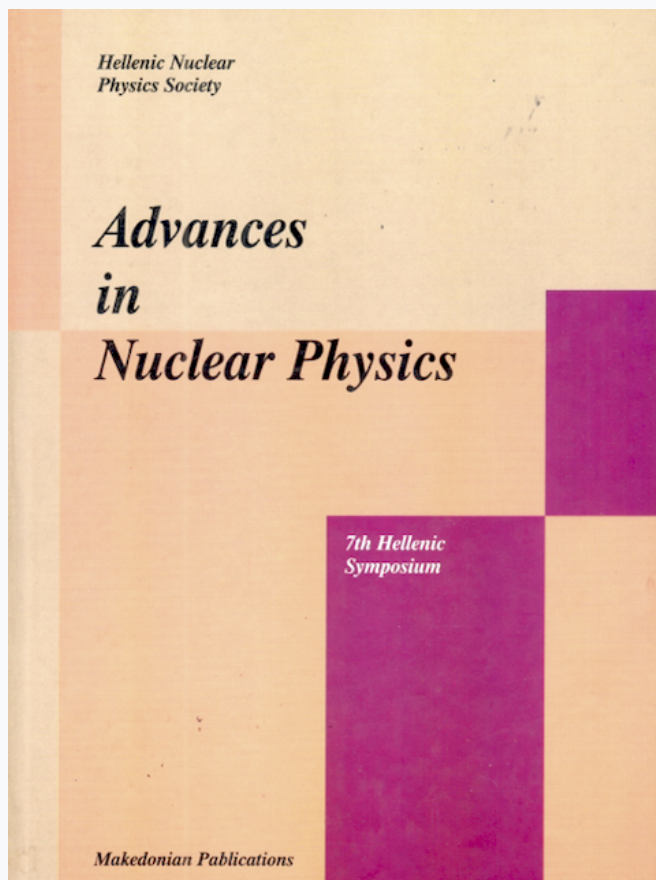


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# Application of Accelerator-based Analytical Techniques to the Study of Geological Materials

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## Abstract

This contribution provides a short presentation of the applications of the most common accelerator-based analytical techniques to the earth sciences. These techniques offer high elemental selectivity and sensitivity as well as the possibility to determine the lateral and depth distribution of the elements under investigation in near-surface layers of geological materials and provide a powerful tool of investigation of geological, mineralogical, geochemical and cosmochemical processes.

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## 1 Introduction

The study of geological materials using accelerator-based analytical techniques is one of the most challenging fields in the modern earth sciences. When high energy particles bombard a target, several types of interactions take place between the projectiles and the target atoms causing the scattering as well as the emission of particles and electromagnetic radiation (X- and  $\gamma$ -rays). These particles and radiations can be used for the identification of the target atoms and the determination of their lateral and depth distribution in the near-surface layers of materials. Table 1 summarises the main features of the most common accelerator-based analytical techniques and gives an overview of their abilities. A detailed description of the individual methods and their applications can be found in a number of reference books (e.g. Deconninck [1], Bird and Williams [2], Tesmer and Nastasi[3], Misaelides [4]). These techniques are complementary to the actual surface analytical methods (e.g. X-ray Photoelectron Spectroscopy, Auger Electron Spectroscopy, Secondary Ion Mass Spectrometry, Low Energy Electron Diffraction), which provide information about the composition of the surface layers of materials (thickness a few Å) and the chemical environment of their constituent atoms. Of especial importance for the earth sciences is the application of the accelerator-based

analytical methods to the investigation of chemically modified mineral surfaces connected to characteristic geochemical processes such as sorption, dissolution and precipitation of secondary phases primarily taking place at the solution-mineral interface (e.g. Hochella and White [5], Stumm [6]). Chemical changes taking place in the near-surface regions of minerals and particularly the resulting elemental depth profiles, play a key role to the identification of the mechanisms of these processes. The literature concerning the application of ion-beam techniques to the study of geological materials is relatively limited, compared to other disciplines (e.g. materials science), although these methods could considerably contribute to the investigation of their constitution and surface properties. This could be attributed to the complexity of the materials, the specialized instrumentation required and the limited access of the earth scientists to accelerator facilities.

**Table 1**

The most common techniques, that can be applied to the characterization and study of geological materials

<b>Ion Beam Analysis (IBA) technique</b>	<b>Radiation measured</b>	<b>Ability</b>
<b>Charged Particle Activation Analysis (C.P.A.A.)</b>	Off-line $\gamma$ -radiation counting	quantitative elemental analysis in the bulk; ppm to ppb sensitivity.
<b>Particle Induced X-ray Emission (P.I.X.E.)</b>	Proton- or charged particle-induced X-rays	quantitative elemental analysis in the bulk; ppm sensitivity; high-resolution mapping possibilities (nuclear microprobe)
<b>Rutherford Backscattering Spectrometry (R.B.S.)</b>	Backscattered projectiles	quantitative analysis of both light and heavy elements; depth profiling; channeling
<b>Elastic Recoil Detection Analysis (E.R.D.A.)</b>	Elastically recoiled target atoms	quantitative analysis of hydrogen and light element target constituents; depth profiling
<b>Nuclear Reaction Analysis (N.R.A.)</b>	Ion-beam induced nuclear reaction products (particles and $\gamma$ -rays)	quantitative analysis of light element target constituents; depth profiling
<b>Accelerator Mass Spectrometry (A.M.S.)</b>	Magnetically separated target atoms	Ultra-high sensitivity analysis (ppb-range); isotopic studies

This contribution presents some selected applications of the accelerator-based analytical techniques to the characterization and study of geological materials.

## 2 The Techniques and their Applications to the Earth Sciences

The CPAA can be considered as the charged particle analogue of the Neutron Activation Analysis (NAA) (s. Vandecasteele [7], Sellschop and Annegarn[8], Tesmer and Nastasi [3]). The samples to be analyzed are bombarded by an ion beam of suitable type and energy. The radionuclides produced during the irradiation by nuclear reactions induced by the projectiles on the matrix itself and/or the impurities of interest are identified and counted mainly using *gamma*-ray spectroscopy. The theoretical basis of the quantitation in the CPAA is based, as in the case of NAA, on the classical activation formula, that can be found in radiochemistry or nuclear physics textbooks. The main difference of the two techniques is the variation of the cross-sections of the charged particle nuclear reactions as a function of the projectiles energy and the energy loss of the charged particles in the matter, which can be turned, in some cases, to an advantage allowing the elimination of unwanted matrix interference (e.g. determination of light elements in a heavier matrix). Although any element can be determined using CPAA by selecting a suitable activation reaction, the technique is especially useful for the determination of trace amounts of light elements (e.g. B, C, N, O, S), that can not easily be determined by conventional analytical techniques or NAA. The P.I.X.E. is the most widely used accelerator-based analytical technique. In the most of the cases the emission of the X-rays is induced by proton beams. The X-ray yield for each element depends on the incident energy of the projectiles. In the beam energy region between 2 and 4 MeV the K-X-rays emitted by the light elements ( $10 < Z < 50$ ) and L-X-rays by the heavier can lead to their identification and quantitative determination. Although the PIXE spectra of geological materials show a complexity of the peaks due to the overlapping of X-rays emitted by the different elements, new spectrum analysis programs enable their deconvolution and the extraction of the quantitative information. Of especial interest is the application of PIXE in dedicated nuclear microprobe facilities, allowing the two- or three dimensional mapping of the elements under investigation in geological matrices. The applications of quantitative micro-PIXE in the earth sciences was reviewed in recent publications (e.g. Sie [9], Ryan and Griffin [10], J.L. Campbell et al. [11]). The number of references in these reviews is indicative of the number of geological and mineralogical applications of the technique. Figure 1 gives an example of application of the micro-PIXE to the investigation of the Hg(II)-distribution on granite minerals (quartz, feldspar and biotite) measured using the proton-microbeam of the University of Bochum/Germany (Misaelides et al. [12]) It is obvious, that the mercury is mainly concentrated on the biotite crystal, whereas the sorption of the element on the other mineral constituents of the quartz is very limited. The dimensions of the analyzed area were in this case  $1 \times 1 \text{ mm}^2$ .

The R.B.S. using ion beams of MeV-energies has been used for the determina-

tion of the stoichiometry, elemental areal density and impurity distribution in near-surface layers of minerals. The measurement of the number and energy distribution of the ions backscattered from the atoms in these layers provides the means of identification of the atomic masses and determination of their distribution as a function of the depth below the surface (s. Chu et al. [13], Leavitt et al. [14]). In the early '90 Cherniak et al. [15] used the R.B.S. for the investigation of the lead diffusion in minerals (apatite). Lead in certain minerals has radiogenic origin and the investigation of its diffusion can considerably contribute to the determination of geochronologic data and interpretation of their thermal history. The same aim had also the investigation of the Sr diffusion in minerals (K- and Na feldspars, anorthite, plagioclase) performed by the same group (Cherniak et al. [16, 17]). The R.B.S. measurements took place after high-temperature thermal treatment of the lead- and strontium-implanted mineral crystals. Vogt et al. [18] also used R.B.S., in combination with P.I.X.E. and P.I.G.E. for the elemental analysis of clinopyroxene specimens.

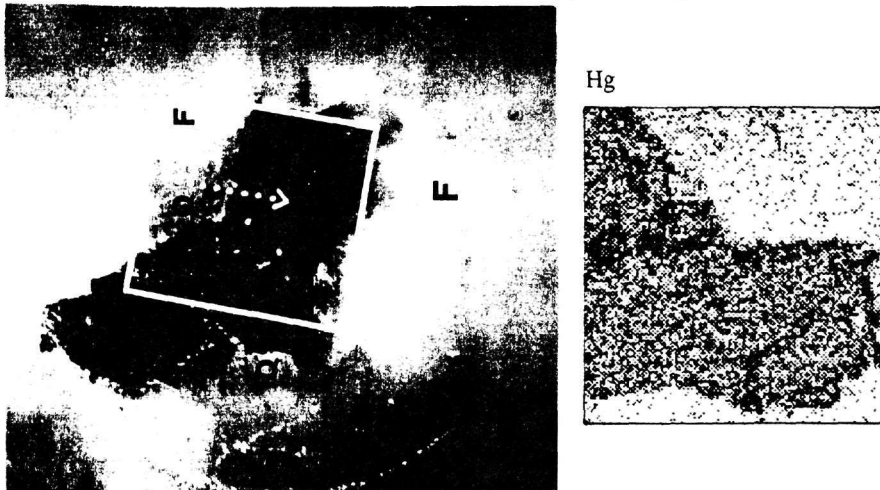


Fig. 1: Microphotographs of selected areas on a polished granite slide studied by micro-PIXE after interaction with Hg(II)-solutions (left part) and the corresponding Hg-distribution maps (investigated are 1x1 mm<sup>2</sup>). Black appearing phase: Biotite, Q: quartz, F: feldspar

One of the most interesting applications of the RBS in the earth sciences is the investigation of deposition and sorption phenomena on mineral surfaces. Dran et al. [19] investigated the sorption of actinide analogues (U(VI), Th(IV), Ce(IV), Ce(III) and Nd(III)) from their aqueous solutions on amorphous silica, granite minerals (quartz, phlogopite and orthose) and calcite using RBS and nuclear reaction techniques. The investigations indicated two possible sorption mechanisms responsible for the elemental partition in the solid/liquid system, namely the incorporation into amorphous hydrosilicates and the precipitation of mixed carbonates. Figure 2 gives the superimposed RBS spectra of Th sorbed on phlogopite showing the irreversibility of the Th retention by this

mineral even by rinsing at 100 °C. Berry et al. [20] studied at the AERE Harwell nuclear microprobe, by a combination of RBS and PIXE, the sorption of uranium and plutonium on rocks and minerals. The energy of the used He<sup>+</sup> beam was 2 MeV and its typical diameter 10 μm. The RBS measurements performed in a particle microbeam facility enabled the determination of the three-dimensional distribution of the elements concerned and lead to the identification of the mineral constituents of the rocks, which are important in their sorption.. The investigations were also complemented by secondary emission mass spectrometry (SIMS) measurements, which are purely surface specific. All these studies are related with the investigation of the environmental behavior of the actinides and their migration in the biosphere (nuclear waste disposal in geological formations).

The use of heavy ion beams for R.B.S. investigations can considerably improve the depth resolution of the measurements, because of the higher energy loss of the projectiles in the host matrix. 12C-RBS was used by Misaelides et al. [21] for the investigation of the Cu-, Hg-, Pb- and U-sorption from aqueous solutions on HEU-type zeolite crystals). XPS measurements were also used in this study in order to determine the chemical form of mercury and uranium species sorbed on the zeolite crystals (s. Fig. 3). The investigation of the chemical processes taking place on the surface of zeolite crystals is of extreme importance, because natural zeolitic materials are utilized for the treatment, immobilization and geologic disposal of industrial and radioactive waste.

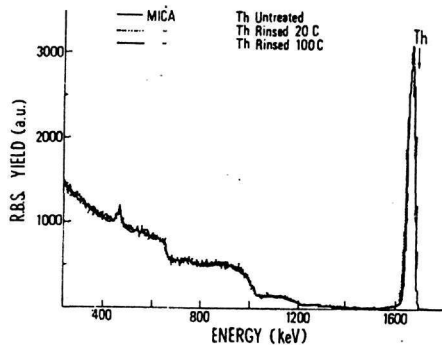


Fig. 2: RBS spectra of sorbed Th on phlogopite showing the irreversibility of the element retention (inefficient rinsing at 20 and 100 °C). The three spectra are completely superimposed (Ref. 19).

In single crystal specimens, the RBS and PIXE spectra can become weaker, if the direction of the incident beam is parallel to one of the main axis or crystal planes. The projectiles pass through the atom arrays in the crystal with coming to direct interaction with them, as in the case of random distribution. This phenomenon is called channeling and can be used in order to distinguish whether an impurity possesses interstitial or substitutional position in the crystal lattice (e.g. Jamieson and Ryan [22]).

The ERDA is a technique complementary to RBS. In this case, the energy distribution of the recoiled (light) atoms, after the collision with much heavier projectiles, provide the quantitative and depth information. A comparison of the experimental set-up of the two techniques is given in Fig. 4. ERDA is important for the determination of the depth distribution of light elements (such hydrogen) in near- surface layers of minerals. Especially interesting is the application of ERDA at a nuclear microprobe facility allowing the three dimensional mapping of the elements under investigation. Sweeney et al. [23] report on the application of the  $4\text{He}$  microbeam (beam dimensions less than  $5 \times 5 \mu\text{m}$ ) of the 6 MV van de Graaff accelerator at the National Accelerator Centre (S. Africa) to the investigation of the hydrogen distribution in a variety of geological materials. The achieved sensitivity for the hydrogen determination was in this case better than 0.04 wt

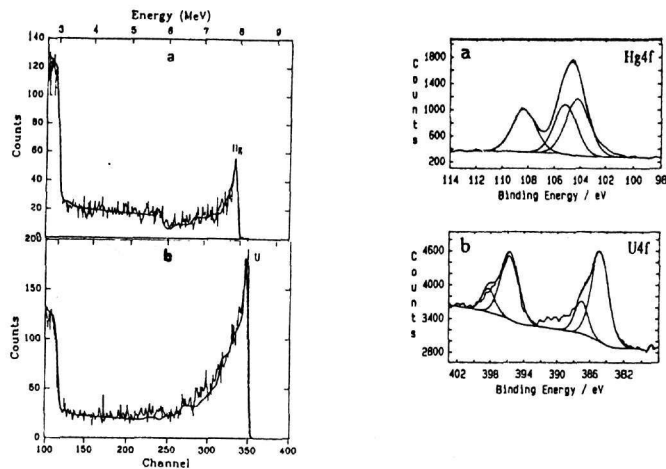


Fig. 3:  $^{12}\text{C}$ -RBS of U- and Hg-loaded HEU-type zeolite samples ((010) cleaved surface) along with the corresponding 4f-XPS spectra indicating the formation of an  $\text{UO}_3$ -type and Hg-oxide/hydroxide phases in the case of U and Hg respectively (Ref. 12).

The N.R.A. is based on the use of a nuclear reaction specific to an isotope of an element, whose concentration and distribution should be determined. The number and the energy particles promptly emitted during bombardment of the target by an ion beam of appropriate energy can provide the means of the quantitative determination of the element concerned and its depth distribution in the near-surface layers of the material. Of especial importance are nuclear reactions exhibiting narrow resonances (Resonant Nuclear Reaction Analysis) in their cross-sections (directly related to the interaction probability), which are preferentially used for depth profiling providing good depth resolution (few nm). Classical examples of RNRA are the nuclear reactions  $^1\text{H}(^{15}\text{N},\text{p}\alpha)^{12}\text{C}$  and  $^{23}\text{Na}(\text{p},\alpha)^{20}\text{Ne}$  reactions allowing the quantitative determination and depth profiling of hydrogen and sodium in minerals. The  $^1\text{H}(^{15}\text{N},\text{p}\alpha)^{12}\text{C}$  reaction

exhibits a sharp resonance at 6.385 MeV with a width of 1.8 keV. This resonance has been used for the investigation of water-rock interactions, which are important in modeling the mass balance of the elements during their geochemical cycle (Petit et al. [24]). The same reaction was also recently applied by Godelitsas et al. [25] to the determination of the structural characteristics of prehnite, a low-subgreenschist facies metamorphic mineral hydrothermally formed in basic igneous rocks. The  $^{23}\text{Na}(p,\alpha)^{20}\text{Ne}$  reaction, which exhibits a narrow resonance (width: 0.6 keV) at 592 keV can be used for the quantitative determination and depth profiling of sodium in near-surface layers of minerals. The depth resolution, that can be achieved by this reaction in common silicate minerals is of the order of 10 nm. A number of other resonant nuclear reactions leading to the emission of  $\gamma$ -radiation (e.g.  $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ ,  $^{30}\text{Si}(p,\gamma)^{31}\text{Si}$ ) or particles (e.g.  $^{18}\text{O}(p,\alpha)^{15}\text{N}$ ) can be applied to the investigation of chemical phenomena (such as dissolution, sorption, precipitation) on mineral surfaces and to the estimation of diffusion coefficients of elements involved in mantle dynamics. The  $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$  reaction was used by Misaelides et al. [26] for the determination of the aluminum depth distribution of acid-treated HEU-type zeolite crystals, which showed a gradual dealumination of their near-surface layers (s. Fig. 5).

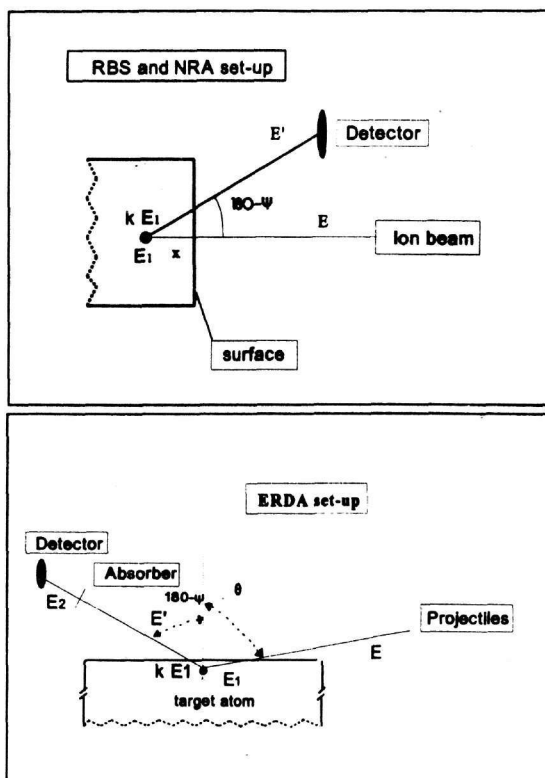


Fig.4: Schematic comparison of the RBS/NRA and ERDA experimental set-up.



The same reaction was used by Gasparik et al. [27] for the investigation of the aluminum diffusion in diopside. On the other hand, the  $^{18}\text{O}(p,\alpha)^{15}\text{N}$  nuclear reaction was used, along with the  $^{30}\text{Si}(p,\gamma)^{31}\text{Si}$ , for the study of the oxygen and silicon diffusion in olivine. The determined diffusion coefficients lead to the identification of the species controlling the rate of the high-temperature creep of olivine in the earth's mantle (s. Petit et al. [24] and Ryerson et al. [28]). The analytical techniques utilizing the prompt  $\gamma$ -ray emission by nuclear reactions are frequently referred as Particle Induced Gamma-ray Emission (P.I.G.E.) in an analogy to the PIXE. The particles inducing the nuclear reactions are not necessarily protons but other particles can also be used for this purpose. For example, Volfinger et al. [29] and Rio et al. [30] used  $\alpha$ -particle beams for the investigation of individual grains of granite minerals as well as volcanic glass inclusions trapped in minerals.

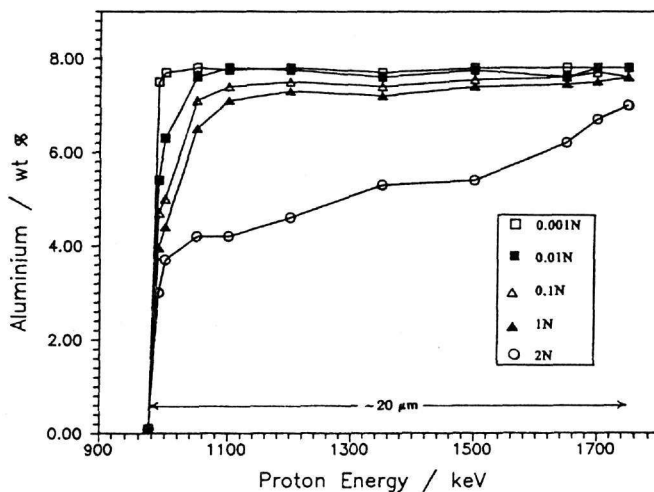


Fig.5: Aluminum depth distribution in near-surface layers of HEU-type zeolite crystals treated by HCl aqueous solutions for 48 h.

Reactions of the proton inelastic scattering type ( $p,p'\gamma$ ) on light elements have also been used for the determination of the Si/Al-ratio in zeolitic materials (Hanson et al. [31]) as well as to the investigation of the sulphur distribution on chemically modified HEU-type zeolite crystals (Godelitsas et al. [32]).

In the AMS the accelerator itself can be used as an ultra-sensitive mass spectrometer. The technique can be considered as a variety of Secondary Ion Mass Spectrometry (SIMS), that uses MeV energies to ensure the total removal of molecular ions from a beam of negative secondary ions generated from a small volume of target material. AMS has become the main method of determination of isotopic ratios and found a variety of applications in earth and planetary sciences. Although the applications of AMS are continuously increasing, a relatively recent presentation of the state of the art in this field is given by Wilson et al. [33].

### 3 Conclusions

Despite of their recent application, the accelerator-based analytical techniques can be considered as valuable tools in the investigation of geological, mineralogical, geochemical and cosmochemical processes. These techniques are being developed and further improvements of their sensitivity as well as their lateral resolution will open new areas of applications in the earth sciences.

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