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PROBING THE ENVIRONMENT WITH ACCELERATOR-BASED TECHNIQUES

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Abstract

Natural and anthropogenic events are deteriorating atmosphere, water, soil and other compartments of our planet. Modern analytical techniques based on particle accelerators can provide useful tools to characterize samples of environmental interest. For example, Accelerator Mass Spectrometry (AMS) is used to detect geological tracers and chronometers, such as ^{14}C , ^{10}Be , ^{36}Cl and ^{129}I , present at ultra-trace level in the environment. These long-lived isotopes are useful to study soil erosion and salinization, ground water management and nuclear waste disposal. Another accelerator-based analytical technique, Synchrotron-Radiation Induced X-ray Emission (SRIXE), can be used to study the microscopic distribution of heavy metals and other trace elements in the environment. SRIXE microprobes are being developed to map trace elements in individual micron-size particles and microorganisms. The principles of these advanced methods and their potential in environmental studies will be discussed.

1. INTRODUCTION

Our environment has always been endangered by natural phenomena: earthquakes, volcanic eruptions, floods, droughts, etc. Increase of population and modern industrialization are more recent causes contributing to the ecological disequilibrium. For example, deforestation and farming practices are contributing to soil erosion. Toxic elements such as heavy metals are introduced into the environment by vehicular traffic and industry.

The advent of novel analytical techniques based on particle accelerators, allowing the measurement of trace and ultratrace elements and isotopes in natural samples, offers new possibilities in environmental sciences.

Accelerator Mass Spectrometry (AMS) is used to measure long-lived cosmogenic isotopes (^{14}C , ^{10}Be , ^{36}Cl , etc.) in samples $10^3 - 10^6$ times smaller than those required for conventional radiometric techniques. New tracers and chronometers are therefore becoming available to study geophysical processes. Successful applications of AMS include erosion and degradation of continental soils [1] and groundwater studies [2,3].

Synchrotron Radiation Induced X-Ray Fluorescence (SRIXE) allows the measurements of trace elements at levels not detectable with traditional analytical techniques. Femtogram quantities of specific elements are detectable with micrometric spatial resolution. For example, single atmospheric particles can be analysed to study the role of heavy metals and other toxic trace elements in environmental pollution.

These are two examples of advanced techniques that are still in the stage of development and assessment. AMS and SRIXE have so far been used mostly in pioneering applications. The full exploitation of accelerators in microanalytical work requires the coordinated effort of workers from physics, environmental science, biomedicine and geology.

In the following sections we first review the origins and fates of cosmogenic radionuclides and the distribution of metals and other trace elements in the environment. Next we outline the principles of AMS and SRIXE. Finally we give some examples of applications of these high sensitivity analytical techniques to environmental problems.

2. LONG-LIVED COSMOGENIC ISOTOPES

Some long-lived cosmogenic isotopes which have been used as chronometers or tracers in studies of terrestrial processes are listed in Table 1. These isotopes are introduced into terrestrial matter by nuclear reactions of the primary and secondary cosmic radiation with target nuclides in the atmosphere, hydrosphere and lithosphere, and by natural radioactivity in the lithosphere [4, 5].

Table 1- Long - lived cosmogenic isotopes

Radioisotope	Halflife [yr]	Range of terrestrial concentration ^{*)}	AMS detection limit ^{*)}
¹⁰ Be	1.6×10 ⁶	10 ⁻⁸ - 10 ⁻¹⁴	10 ⁻¹⁵
¹⁴ C	5.7×10 ³	10 ⁻¹² - 10 ⁻¹⁶	10 ⁻¹⁶
²⁶ Al	7.2×10 ⁵	10 ⁻¹² - 10 ⁻¹⁵	10 ⁻¹⁵
⁶ Cl	3.1×10 ⁵	10 ⁻¹² - 10 ⁻¹⁶	10 ⁻¹⁵
⁴¹ Ca	1.0×10 ⁵	10 ⁻¹³ - 10 ⁻¹⁶	10 ⁻¹⁵
¹²⁹ I	15.9×10 ⁶	10 ⁻¹² - 10 ⁻¹⁶	10 ⁻¹⁴

*) Compared to the stable isotope of the same element

2.1 Atmospheric production

¹⁰Be is produced in the atmosphere primarily by spallation reactions induced by high-energy cosmic rays on oxygen and nitrogen.

¹⁴C is produced mainly by (n,p) reactions on atmospheric ¹⁴N.

²⁶Al is produced in the atmosphere by spallation of Ar.

³⁶Cl is produced by the cosmic-ray spallation of ⁴⁰Ar and the reaction ³⁶Ar(n,p)³⁶Cl. ³⁶Cl was also produced by the nuclear tests performed from 1953 to 1957 in the atmosphere through the reaction ³⁵Cl(n,γ)³⁶Cl in sea-water.

¹²⁹I is produced by spallation of atmospheric xenon. Nuclear bomb tests and nuclear reactor emissions have been other sources of ¹²⁹I.

2.2 Lithospheric production

Cosmic rays produce radionuclides in the upper 3-4 m of the earth's crust through spallation and neutron-capture reactions by primary and secondary cosmic-ray particles. At greater depths, from 10³ to 10⁵ g/cm², production by cosmogenic muons can be significant. Natural radioactivity, mainly derived from U and Th, can also produce significant amounts of some isotopes, by α-particle or neutron induced reactions.

¹⁰Be is produced directly at the earth's surface mainly by cosmic-ray spallation of oxygen. The reactions ¹²C(n,3He) and ¹³C(n,α) are also important in carbonate rocks. At greater depths production by muon spallation of oxygen predominates. Radioactivity can produce significant amounts of ¹⁰Be by the above neutron reactions. The contribution of lithospheric production of ¹⁰Be to the terrestrial inventory is small compared with atmospheric production.

²⁶Al is produced by cosmic-ray spallation of Si, Al, and Fe.

³⁶Cl is produced by low-energy neutrons through the reaction ³⁵Cl(n,γ)³⁶Cl and from spallation reactions on K and Ca. At a depth of several meters in the lithosphere production of ³⁶Cl is dominated by muon reactions.

¹²⁹I is produced in uranium-bearing rocks by spontaneous fission and (α,n) induced

fission. Lithospheric and atmospheric contributions to marine ^{129}I are probably comparable.

2.3 Precipitation, transport and storage

^{10}Be is transported to the Earth's surface by rain or snow in a few weeks and accumulated in a chronological sequence in polar ice ($10^4 - 10^5$ atoms/g), marine sediments ($10^9 - 10^{10}$ atoms/g) and soils ($10^7 - 10^8$ atoms/g).

Some of these collectors can be dated by independent techniques. Ice chronology is obtained from seasonal cycles; sedimentation rates and ^{14}C are used to provide ages of sediments. Measurements of ^{10}Be concentration in these archives allow the observation of variations in production rates induced by changes in solar activity and geomagnetic excursions. The ^{10}Be content in these reservoirs is also modulated by climatic changes in the past and other factors influencing transport and deposition. Polar ice is an archive of this isotope extending back in the past for $10^4 - 10^5$ yr and ^{10}Be can be measured with high temporal resolution (10 - 100 yr). The present accumulation rate of ice in Antarctica is about 14 cm of water-equivalent per year. Cores of about 2000 m depth are drilled and 1 kg of ice is sufficient to measure ^{10}Be with AMS.

The ^{14}C produced in the atmosphere quickly combines with oxygen to form CO_2 , and hence it has a long residence time in the atmosphere. Exchange between oceanic and atmospheric reservoirs of CO_2 buffers the atmospheric ^{14}C concentration. Atmospheric $^{14}\text{C}/^{12}\text{C}$ ratios are therefore quite uniform world-wide. ^{14}C is useful especially for dating of biogenic materials. In-situ production of ^{14}C typically limits its usefulness to roughly 5×10^4 yr.

^{26}Al produced in the atmosphere attaches quickly to atmospheric particulates or aerosols. Particles are scrubbed from the atmosphere on a time scale of a few weeks. Since ^{10}Be and ^{26}Al have similar, lithophile geochemical behaviours, they tend to be precipitated together. Hence the $^{10}\text{Be}/^{26}\text{Al}$ ratio is less sensitive to changes in non-chronological factors than the absolute concentration of either one.

The total fallout rate of ^{36}Cl corresponds to a production rate of $5-30 \text{ at m}^{-2} \text{ s}^{-1}$ [4]. The $^{36}\text{Cl}/\text{Cl}$ ratio in the atmosphere is highly variable, depending on latitude and distance from the sea. Near the sea, atmospheric Cl mixes with Cl from ocean spray, which has a very low $^{36}\text{Cl}/\text{Cl}$ ratio. As a result, the $^{36}\text{Cl}/\text{Cl}$ ratio increases by as much as two orders of magnitude from the seacoast to mid continent.

Chlorine is a hydrophilic element with a long residence time in water as a dissolved anion. ^{36}Cl is therefore a good candidate for use as a groundwater tracer.

Like Cl, I is geochemically very mobile in its inorganic form. Hence, ^{129}I should also be useful as a groundwater tracer. Its half-life of 16 Myr allows it to be used in applications involving much larger timescales than ^{36}Cl . The ratio $^{129}\text{I}/^{127}\text{I}$ in pre-bomb marine sediments is about 10^{-12} [6], which is readily measurable using AMS.

3. TRACE ELEMENTS

A trace element may be operationally defined as any element having an abundance less than about 100 ppm. The abundances of elements in average crustal rocks are listed in Table 2 [7]. Various geochemical and geophysical effects influence the geological distribution of these elements: metamorphism, climatic factors, volcanic eruptions, etc. While the values in Table 2 represent average crustal abundances of the elements, local enrichments of individual elements by many orders of magnitude occur in ore minerals.

Table 2 - Average crustal abundances of the elements (in ppm) [9]

Element	Crustal average	Element	Crustal average
H	1,400	Rh	0.005
Li	20	Pd	0.01
Be	2.8	Ag	0.07
B	10	Cd	0.2
C	200	In	0.1
N	20	Sn	2
O	466,000	Sb	0.2
F	625	Te	0.01
Na	28,300	I	0.5
Mg	20,900	Cs	3
A	181,300	Ba	425
Si	277,200	La	3
P	1,050	Ce	60
S	260	Pr	8.2
Cl	130	Nd	28
K	25,900	Sm	6.0
Ca	36,300	Eu	1.2
Sc	22	Gd	5.4
Ti	4,400	Tb	0.9
V	135	Dy	3.0
Cr	100	Ho	1.2
Mn	950	Er	2.8
Fe	50,000	Tm	0.5
Co	25	Yb	3.4
Ni	75	Lu	0.5
Cu	55	Hf	3
Zn	70	Ta	2
Ga	15	W	1.5
Ge	1.5	Re	0.001
As	1.8	Os	0.005
Se	0.05	Ir	0.001
Br	2.5	Pt	0.01
Rb	90	Au	0.004
Sr	375	Hg	0.08
Y	33	Tl	0.5
Zr	165	Pb	13
Nb	20	Bi	0.2
Mo	1.5	Th	7.2
Ru	0.01	U	1.8

Industrial civilization depends on ore minerals to supply certain otherwise trace metals for a wide variety of uses. Global production of some of the most important ones for the year 1981 are reported in Ref. [8]. From a geochemical stand-point, these quantities represent the mobilization and dispersion of metals in the environment. Having been concentrated by natural processes over geologic time in unusual, sparsely distributed ore bodies, they are now being redistributed at much reduced concentrations, which nonetheless may locally exceed by orders of magnitude their average crustal abundances.

Trace metals have high concentrations in atmospheric dust and aerosols. It is suspected that the enrichment of these metals in atmospheric particulates is related to biological affinity [9].

In general, there is a growing interest and awareness about the role of trace elements in the functioning of living systems.

4. ACCELERATOR MASS SPECTROMETRY

AMS is an analytical technique that uses an ion accelerator and its beam transport system as an ultra-sensitive mass spectrometer to provide several stages of mass analysis and element (Z) identification in the final detector [10]. AMS has been successfully employed in the analysis of long-lived cosmogenic radioisotopes present in natural samples with isotopic ratios relative to the principal stable isotope of 10^{-9} - 10^{-16} [11]. The factors determining the selectivity, precision and sensitivity of the technique are detailed in the following sections.

4.1 Selectivity

The backgrounds that plague conventional mass spectrometers are reduced in AMS in several ways. Molecular interferences are eliminated by analyzing ions in the 3+ or higher charge state. Elemental isobars are more difficult to eliminate and several different approaches have been adopted:

- i) At the ion source. The competing isobar is eliminated when it does not form negative ions (e.g. ^{14}N vs ^{14}C).
- ii) Range separation. When the interfering isobar has a higher Z than the rare isotope (e.g. ^{10}B vs ^{10}Be), it loses energy faster when passing through matter and can be made to stop in a thick adsorber placed in front of the detector, while the isotope of interest passes through.
- iii) Complete stripping. At sufficiently high energies, all electrons can be removed leaving the bare nucleus. Isobaric interferences can be completely eliminated by subsequent magnetic analysis if the interfering isobar has a lower Z than the rare isotope.
- iv) Particle identification. The particle detectors employed in AMS are able to identify the

Z of the incoming ion if it enters with an energy above the Bragg peak. The energy, specific energy loss, and range in the ion counter provide parameters for discriminating against isotopes and isobars .

- v) Gas filled magnet. Charge changing collisions of an ion traveling through a gas result in an average charge state that depends on the Z of the ion. Since the trajectory of an ion in a magnetic field depends on its charge, ions with different average charges will follow different trajectories resulting in isotope separation.

Of the foregoing list of approaches, particle identification and the breakup of molecules are the most generally applicable and contribute the most to the high abundance sensitivity of AMS.

4.2 Precision

The isotopic ratios measured by AMS are typically less precise than those obtainable with conventional mass spectrometers. In general, precision depends on counting statistics and corrections for isotopic fractionation and blank corrections. A precision of better than 1% is obtained at dedicated AMS facilities in the measurement of ^{14}C [12]. More typically, isotopic ratios are measured with an uncertainty of 3-10%. The precision is limited by the complicated beam optics of AMS systems and/or the small number of ions counted.

4.3 Efficiency

The efficiency of an AMS system is the ratio of the number of atoms (of interest) counted in the detector to the number loaded in the ion source. This ratio is the product of

- i) the negative-ion formation efficiency,
- ii) the probability of forming the analyzed charge state,
- iii) the efficiency of transporting the beam from the source to the ion counter and
- iv) the detection efficiency. The overall efficiencies of AMS systems range from 1% for ^{14}C detection to 0.02% for ^{129}I detection.

4.4 Background

Backgrounds include all signals in the final detector that cannot be separated from those corresponding to the nuclide of interest. They include:

- i) backgrounds deriving from the limited resolution of the ion detector in the measurement of energy, velocity and specific energy loss,
- ii) cross contamination with other samples in the ion source,
- iii) ion-source background and
- iv) contamination before or during sample preparation.

5. SYNCHROTRON RADIATION INDUCED X-RAY FLUORESCENCE

Several analytical methods have been developed in recent years to detect trace elements of interest in environmental sciences.

Nuclear and atomic techniques have the advantage of allowing fast, non-destructive and multielemental analyses. Successful results have been obtained with methods based on the measurement of characteristic X-rays (XRF: x-ray fluorescence) emitted by the element of interest.

The use of Synchrotron Radiation (SR) for XRF allows measurements of trace elements at the ppb level. The properties characterizing SR as a unique fluorescence source are: tunability of the energy, high brilliance and polarization of X-rays.

The high intensity of SR beams can be exploited to develop X-ray fluorescence microprobes for multi-elemental imaging with micron-resolution [13]. A number of techniques are available to produce X-ray microbeams. Collimation of the white beam from a SR bending magnet has been successfully utilized at beam-line X-26, Brookhaven National Laboratory [14]. Some results obtained with this system are shown in Figures 1 and 2. In other cases, wide-band optical systems based on multilayer mirrors [15] and bent crystals [16] have been adopted.

New synchrotron radiation microscopes based on X-ray fluorescence for advanced applications in natural sciences are being proposed at third generation SR facilities [17]. These SR sources are characterized by a high number of photons/second/solid angle/source area and are capable of better performance than existing machines for the operation of a microbeam.

6. APPLICATIONS

The analytical techniques described in the previous sections can be used for high-sensitivity measurements of natural tracers and environmental pollutants. Some applications to specific problems will be briefly discussed in the following examples.

6.1 Atmosphere

6.1.1 Pollution.

The study of atmospheric particles (1 - 100 μm) is very important for understanding environmental pollution. The correlation between chemical composition and particle size is important for studying the damage induced by respirable dust particles. Individual flyash particles emitted from coal-fired power plants have been recently characterized using the Brookhaven SRIXE microprobe [18]. Fig. 1 shows an example of multielemental imaging obtained at beamline X-26 (NSLS) on a section of a flyash particle (diameter about 100 μm)

from an Italian power plant.

6.1.2 Climate.

There is strong evidence that the Earth's climate is modulated by atmospheric aerosols and particles [19]. For example, anthropogenic, volcanic and extraterrestrial materials have been implicated in the depletion of the ozone layer [20]. Single particles directly collected in the stratosphere can be analyzed with a microprobe based on synchrotron radiation. In addition, volcanic particles in ice are a clue to the type of volcanism occurring at a specific time. Chemical analysis of trace elements on individual particles using a SRIXE microprobe can be used for the study of the relationship between volcanism and atmospheric temperature.

6.2 Soil

Erosion and weathering of soils is a dramatic problem for many areas of our continents. Agriculture is based on the topsoil, a very precious and non-renewable resource.

In the last few years, there have been some pioneering studies of erosion based on ^{10}Be produced in the atmosphere and in-situ, in the upper layers of soils and rocks [1].

^{26}Al produced in-situ in surface rocks has been detected using AMS. In well-characterized samples of known exposure conditions and unaffected by leaching, it can be used to determine rates of erosion, uplift or subsidence, etc.

6.3 Groundwater

^{36}Cl and ^{129}I can be used to infer age and travel time of old groundwater. ^{36}Cl has been already applied to study the Great Artesian Basin and Murray Hill basin in Australia [2,3.]. However, groundwater often exchanges Cl and I with the surrounding rock by dissolution of salts or ion filtration in compacted shales and clays [6]. In U-bearing host rocks (e.g. shales and granites), leaching of in-situ produced ^{36}Cl and/or ^{129}I can be significant, complicating the interpretation of $^{36}\text{Cl}/\text{Cl}$ or $^{129}\text{I}/^{127}\text{I}$ profiles in a formation [6]. For this reason it is important to measure these isotopes in conjunction with other modes of investigation in order to arrive at a correct understanding of the hydrologic properties of a given system.

6.4 Hydrosphere

6.4.1 Pollution

The Mediterranean Sea is suffering from the pollution induced by agricultural and industrial activity. For example, heavy metals are destroying the equilibrium between algae and bacteria. The effect of this pollution became evident during recent years in the abnormal production of *Pinnularia* at the surface of the Adriatic Sea. The detection of ion location in algae is useful to understand the role played by toxic elements in various biochemical

pathways. Fig. 2 is an example of elemental imaging obtained at the X-26 microprobe from a thin section (5 μm) of a red algae (*Gracilaria*) from the Adriatic Sea.

6.4.2 Oceanography

Measurement of ^{14}C and other anthropogenic tracers in sea water is of paramount importance to provide constraints on ocean circulation models. The development of these models is essential for accurate prediction of future climatic changes. Only AMS will provide the capability of measuring the 10,000 - 20,000 small volume radiocarbon samples required for hydrographic surveys.

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FIGURE CAPTIONS

Figure 1 - SRIXE elemental images obtained from a single two-dimensional scan of a thick section of a flyash particle. Color spectrum reveals elemental concentration (black = minimum, white = maximum). Beam size = $5\ \mu\text{m} \times 5\ \mu\text{m}$, pixel size = $7\ \mu\text{m} \times 7\ \mu\text{m}$, scan area $175\ \mu\text{m} \times 133\ \mu\text{m}$, acquisition time per pixel = 15 s.

Figure 2 - SRIXE elemental images from a thin section of a red algae (*Gracilaria*). Beam size = $5\ \mu\text{m} \times 5\ \mu\text{m}$, pixel size = $8\ \mu\text{m} \times 8\ \mu\text{m}$, scan area $336\ \mu\text{m} \times 240\ \mu\text{m}$, acquisition time per pixel = 15 s.

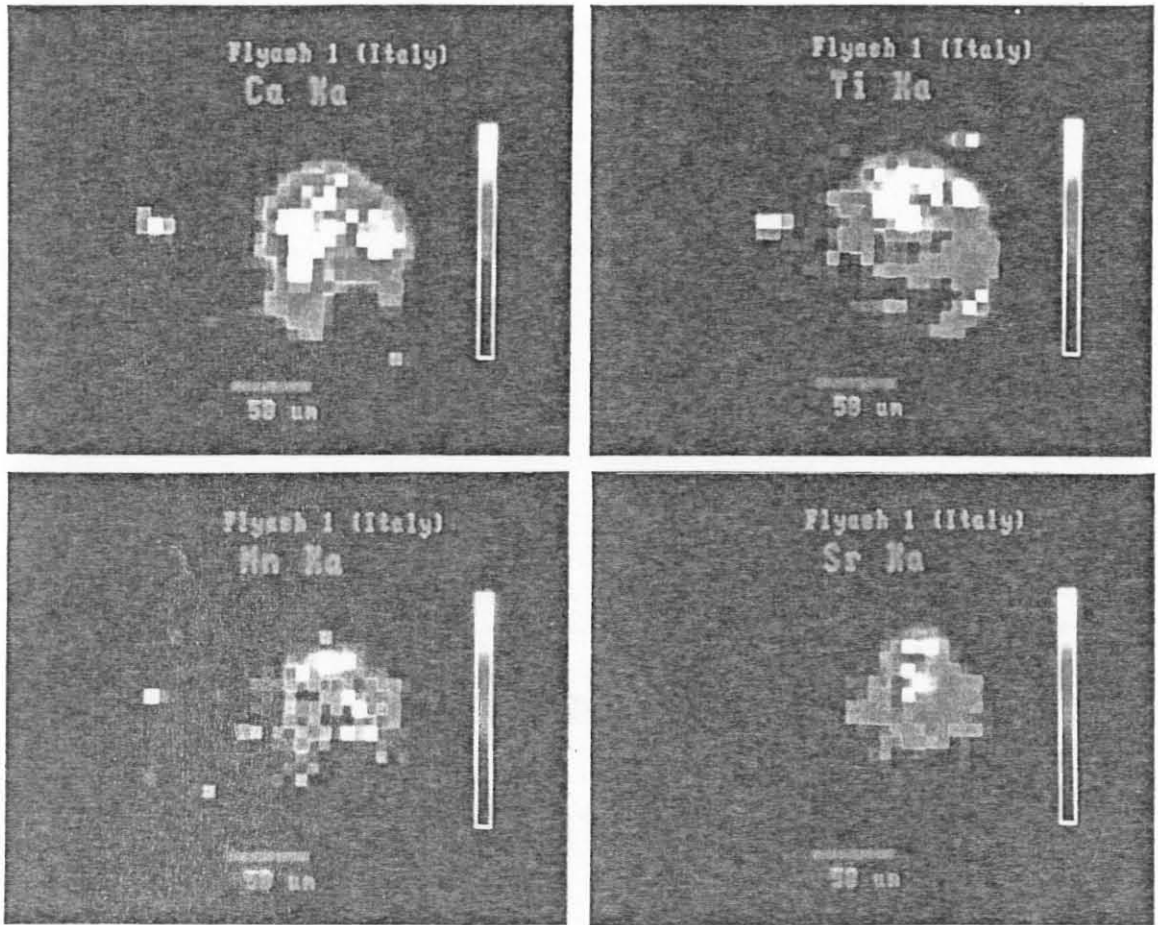


FIGURE 1

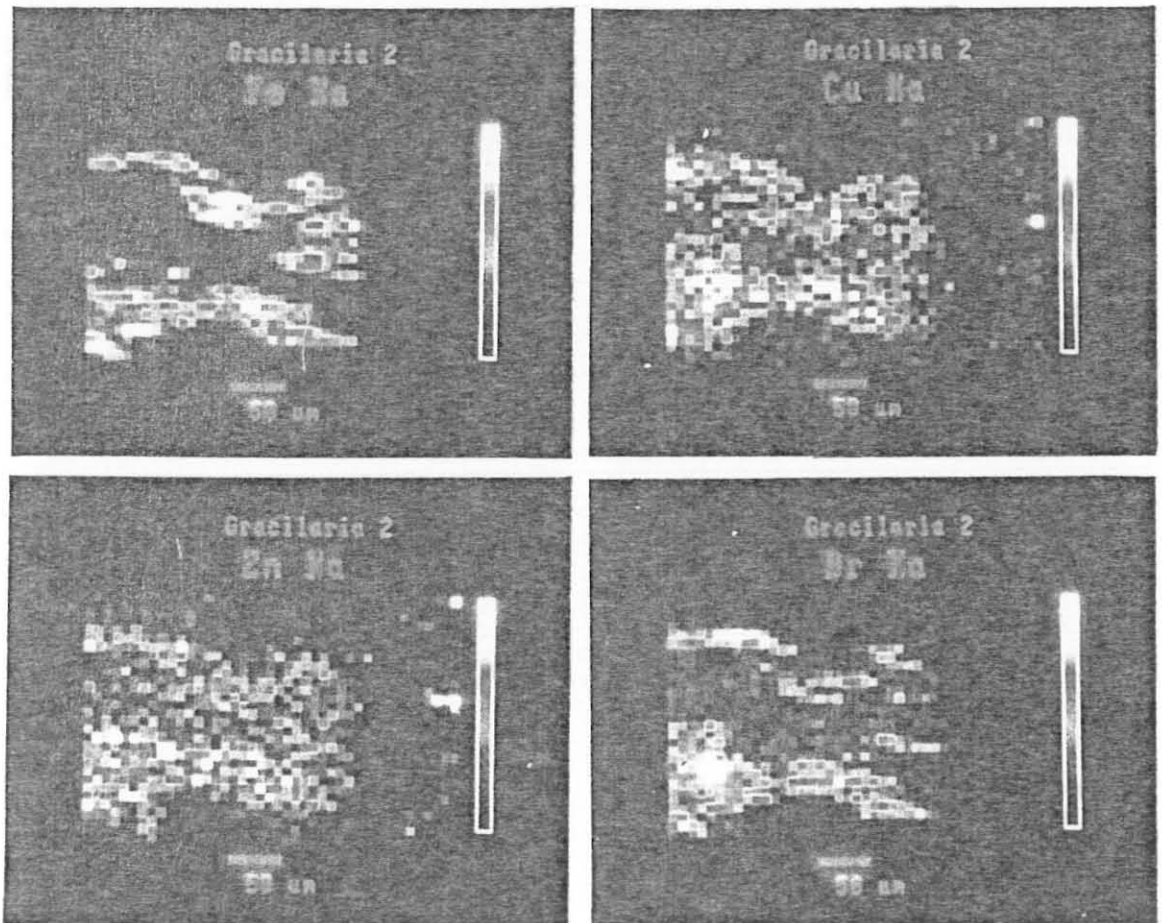


FIGURE 2