Applying MeV ion beam techniques to geochemical issues: cross-fertilizing nuclear physics and geosciences

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Important breakthroughs have occurred in the geosciences (as well as in the environmental sciences) since the sixties notably in direct connection with the extensive use of increasingly sophisticated physical and chemical techniques. These techniques were in great part derived from other fields such as nuclear physics, materials science, physical-chemistry, etc. To name only but a few, let us recall the key role played in this context by the electron microprobe, XPS, SIMS, X-ray spectrometry, RMN, Mössbauer, neutron activation, etc. Usually, the delay necessary to 'import' such sophisticated techniques from one field to another is of about 5 to 10 years. During the last decade or so, a few research groups around the world have systematically applied a new type of analytical tools to geochemical issues. A range of techniques based on the use of energetic ion beams produced by small MeV-accelerators as probes for investigating the near-surface regions of solids (both crystalline minerals and glasses) has thus made a remarkable contribution to geoscientific issues (nuclear microanalysis). These techniques are essentially the now quite classical PIXE (and complementary techniques), the Rutherford Backscattering Spectrometry (RBS), the Nuclear Reaction Analysis (NRA) and the Elastic Recoil Detection Analysis (ERDA).

Interestingly enough, these tools have been first developed and used in materials science when, during the 70's, small MeV particle accelerators have been slowly deserted by nuclear physicists who needed ions of increasingly higher energies to perform their experiments. In order to avoid the closing down of these facilities, research centres around the world have had to try and find new applications outside nuclear physics. This implied to first conceptually realize that MeV ion beams produced by these accelerators could be used not only as a bombarding tool to induce nuclear reactions but also as a probe of the chemical characteristics of the near-surface of solids. Scientists involved in the 'conversion' of these small accelerators have had to identify and measure the specific nuclear parameters which were needed, and in general not available, for this very particular application of ion beams (e.g. cross sections, energetics of resonant nuclear reactions, stopping power in solids of interests, etc.). In order to leave nuclear physics, these scientists had to do more nuclear physics Finally, they had to apply these emerging techniques to issues in materials science and to convince their colleagues in this field that energetic ion beams could make significant, and in some cases unique, contributions. RBS has been the first technique to be used. Latter on, nuclear reactions have been applied The few research centres who have been successful in this cross-fertilization between nuclear physics and materials science have indeed participated to a kind of analytical revolution where both instruments and techniques as well as their scientific applications have been simultaneously developed.

During the 80's, a small number of research groups around the world realized that minerals, and more broadly geological solids (including those used for archaeological artifacts), were not basically different from technological materials. In addition, many issues in geochemistry concern interfaces (e.g. the solid/solution interface) and it was soon realized that these ion beam techniques, allowing the detailed investigation of the near-surface regions of solids at a micrometre scale, were ideal tools. A number of applications in geochemistry have been developed during the past decade (and are still under development), which can be classified into three basic categories:

1. Implementation of ion beam analytical techniques for the study of either trace elements distribution ('microprobe' function such as for instance PIXE) or interface processes ('depth profiling' function such as RBS, NRA, ERDA, etc.).

2. Simulation of natural irradiation linked to alpha-decay, fission fragements, neutron irradiation, etc.

3. Incorporation of impurities or depth markers for diffusion studies or researches on processes involving surface recession (e.g. aqueous

dissolution, sputtering, etc.).

In fact, the first category of applications has been extensively developed whereas the two others have been used only in a much more limited number of works. However, in this lecture, we will cover the above three applications which will be illustrated by outstanding investigations carried out in recent years in geochemistry. We will identify the potential of these techniques, specify their advantages and limitations, and suggest possible future extensions. We will show that applying such techniques in geochemistry leads to the development of facilities were nuclear physics and geosciences are cross-fertilized.

Energetic ion beam analysis

The use of these techniques in geochemistry stems from the fact that the bombardment of solid surfaces with energetic ion beams induces the emission of a characteristic signal which allows: 1) Microanalysis of elements in materials of interest in geosciences. Such an analysis provides a finger print characteristic, notably for trace elements, of the history of these materials. 2) Depth profiling of major and minor elements in the near- surface region of solids, from which one can infer the mechanisms of interface phenomena involved in many important issues such as water/rock interactions, behaviour of inorganic pollutants in the biosphere and the geosphere, etc.

In fact, four analytical techniques are now used in geosciences, the basic underlying physical principles of which will be described: 1) Particle induced X-ray emission (PIXE); 2) Rutherford Bascattering Spectrometry (RBS); 3) Nuclear Reaction Analysis (NRA) and 4) Elastic Recoil Detection Analysis (ERDA). The advantages of these techniques with respect to more classical ones of current use in geosciences are essentialy that they are quantitative, non destructive, not affected by any matrix effect and that they allow the depth profiling of elements with a very good depth resolution ranging from 3 to 30 nm. However, they suffer from notable limitations. First of all their lateral resolution, until recently, was poor (of the order of a mm). This situation is now rapidly changing through the development of microbeam devices on the best facilities. Another limitation stems from their sensitivity which currently ranges from 0.1 to 1%, with the exception of PIXE which is a highly sensitive technique. In addition, and contrary to other techniques of common use in geosciences (e.g. XPS, X-ray spectrometry), no information on structure or chemical state can be obtained. A final limitation stems from the fact that, in most cases, only model materials (large samples, polished or cleaved surfaces, etc.) can be investigated.

Examples of current applications of these techniques, as well as of possible future developments, deal with water/rock interactions, mantle dynamics and environmental issues. Indeed, these techniques have been first extensively used to investigate the mechanisms governing mineral and glass dissolution- More broadly, future developments would deal with linking such local mechanisms with global geochemical cycles of elements. Moreover, issues related to elemental mineralization processes, including the formation of metallic ore deposits, could be tackled. Second, nuclear microanalysis has been used for contributing to the determination of the mechanisms of mass transfer in the Earth's mantle: diffusion of constituent elements, creep of minerals and kinetics of solid state mineralogical reactions used as geothermobarometers. Third, ion beam analytical techniques are currently applied to address issues relevant to the disposal of radioactive waste in geological formations and to other topics linked to the dispersion of a variety of pollutants in the environment. In particular, the corrosion of radioactive waste matrices, and the subsequent possible migration of radioelements in the geosphere has led to a large number of publications.

Simulation of natural irradiations

This second category of applications has been far less developed than the previous one but its potential for particular problems should not be neglected. Indeed, ion/solid interactions occur for instance in minerals containing actinide elements such as uranium and thorium (or in contact with such radioelement-containing minerals). An intensive ion bombardment, by spontaneous fission and/or alpha-decay, can induce important transformations in materials of geological significance, notably with respect to structural properties, physical properties (optical, mechanical) and chemical properties. Metamictization is, for instance, the ultimate state of mineral alteration due to self-irradiation. It has been advocated as a possible cause for the initial release of these elements in groundwater in favourable conditions and, hence, as the primary step of some uranium ore formations. This phenomenon should also be considered in relation with geochronology since it can accelerate the differential diffusion of elements outside mineral structures. Finally, it is of particular concern for the prediction of the behaviour of radioactive waste forms (high-level nuclear glasses and ceramics) upon damage mainly due to α-decay.

In fact, the slowing down of ions in solids proceeds via two processes based on coulomb interaction: 1) Elastic collisions with nuclei (dominant at low energy); 2) Inelastic collisions due to interaction with electrons (dominant at high energy). Important effects and parameters, including nuclear and electronic stoppings, ion ranges, defects distribution, defects combination (extended defects), amorphisation, etc., can be studied in great detail thanks to ion bombardment with MeV accelerators in order to fully understand these processes and to properly calibrate simulations intended to investigate natural irradiations.

Of course, the validity of using external ion beams for simulating natural irradiations has been highly debated in the 80's. Arguments based on structural (defect structure in ion-bombarded and self-irradiated minerals) and physico-chemical grounds (enhanced dissolution rate in metamict, neutron-irradiated and ion-bombarded minerals) demonstrate that external bombardments are useful and very versatile tools.

Ion implantation

This aspect of the use of ion beams has been treated yet in a limited number of works. However, it has already been demonstrated that ion beams can be used for doping a wide variety of solids with impurities for laboratory experimentation in view to quantify elemental transfer mechanisms of geological significance. Applications concern first radiochronology where the knowledge of the diffusion coefficients of long-lived radionuclides and their daughters in minerals is important for modelling open systems and correct absolute ages Second, contributions can be expected in kinetic geochemistry where the study of the aqueous corrosion of minerals with very slow kinetics, which occurs, in particular, under near-equilibrium conditions, is difficult with current analytical techniques. An original approach stems from the possibility to measure very small surface recession by doping the mineral, via bombardment, with heavy ions which are used as a depth marker.

The future developments of these techniques might occur along three lines of research and development:

1. The implementation of the microbeam technology on the facilities. This is a very important point since many applications in geosciences were indeed hampered until recently by the poor lateral resolution of these techniques. In particular, the direct and in situ analysis of minerals in rocks was, in practice, not possible due to their commonly very small size. The use of the techniques was thus, in most cases, restricted to model mineral systems of great size (typically cm-sized) and to laboratory experiments in contrast to direct investigations of geological materials which is, indeed, what geoscientists usually need to do. As for other techniques, this will imply the development of devices allowing the precise localization of the beam on the sample surface with a precision good enough to investigate the multi-phased geological objects.

2. The increase of the analytical capabilities of these techniques which implies in particular the study of new nuclear reactions. In effect, only a few of them have been investigated and systematically used as yet and the analysis of a great number of elements in the periodic table, including light and heavy elements, has still to be developed. This notably implies the exploration of nuclear reactions at higher energies than those used so far for instance for lighter elements (e.g. carbon). In addition, the extention of RBS by the use of more energetic beams would also be very useful. Finally, the increase of the analytical capabilities could originate from improvements in the detectors sensitivities and/or implementation of specific techniques (e.g. coincidence).

3. The integration of several (if not all) of these techniques into a single MEV ion beam facility which would allow to combine their respective analytical potentialities for the investigation of a given sample. This combination already exists (or is currently under development) in a limited number of facilities and is then commonly called the 'Nuclear microprobe'.