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MICRO-PIXE (PARTICLE-INDUCED X-RAY EMISSION ANALYSIS) APPLICATIONS IN MINERALS RESEARCH

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Abstract

The versatility of the PIXE method with microbeams of protons as a non-destructive, in-situ probe for trace element analysis in the geosciences has been demonstrated in an ever increasing number of cases. While in most applications the method can be considered as derivative or as an extension of electron microprobe methodology, features unique to the proton microprobe enable new approaches to hitherto intractable problems of analysis. An appropriate niche has been established in igneous mineralogy and petrology, with important implications both in the basic geosciences as well as mineral industry applications, particularly in the diamond exploration industry. This paper reviews recent advances and discusses the advantages and limitations of current micro-PIXE applications in the geosciences in view of other competing and complimentary methods.

Introduction

Microbeam methods in the geosciences have expanded rapidly within the past two decades, adding new dimensions to established methodology and opening up new areas of investigation. Much of the progress is due to the fact that detailed analysis can be carried out on monomineralic grains, the basic constituent of all geological samples. With micrometre size probes chemical composition can be obtained on microstructures associated with the generation and subsequent alteration of the minerals. The electron microprobe has been responsible for identification of many new minerals, with its prime capability of in-situ non-destructive elemental analysis of the major and minor elements, and trace elements at concentrations above 500 ppm. Secondary ion mass spectrometry (SIMS) with ion microprobes is traditionally a tool for isotopic geochemistry and geochronology, but is now also used as a trace analyzer [Reed 1989]. A newcomer into the field is the synchrotron radiation probe [Bos et al., 1984]. The proton microprobe [Cookson et al., 1972, 1976] has also been in existence for two decades and its applications in minerals research and in other areas [Cahill, 1980] are expanding rapidly.

Applications of proton microbeam methods have developed along two separate lines, similar to the development of electron beam methodology. In one the emphasis is on imaging applications and spatial resolution is usually the driving force behind its development, akin to the scanning electron microscope (SEM) development. The other mode concentrates on quantitative analysis, usually directed towards obtaining the best sensitivity for elemental analysis, akin to the electron microprobe (EMP). With the much lower level of accompanying background continuum radiation, particle induced X-ray emission (PIXE) [Johansson et al, 1970, 1976, Folkmann et al 1974] offers a sensitivity as much as 100 times better than electron induced X-ray spectroscopy. The proton microprobe can also be used for Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA) [Toulhot et al. 1991, Courel et al. 1991]. When gamma rays are detected the method is known as PIGME - particle induced gamma ray emission, which is used mainly to detect low Z elements (e.g. F with ppm sensitivity [Bird and Clayton 1983]). Microbeams of

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particles other than protons have also been applied to geological problems. Alpha beams have been used to determine H content of melt inclusions by the elastic recoil detection method [Mosbah et al. 1991], and deuteron beams have been used to determine C distribution in chondrites [Makjanic et al. 1991]. The present review relates to the application of PIXE with a microbeam as an in-situ analytical method for quantitative trace element analysis on micrometre size samples in minerals research.

Mineral composition is the basis of geochemistry: in petrology and ore mineralogy it can reveal the more subtle ("cryptic") signatures of the geological processes involved in their genesis. Partitioning of major and minor elements between the melt and crystallizing phases is known to be affected by the composition of the parent magmas, wallrock interactions, the presence of volatiles and the ambient pressure and temperature. Incompatible elements, occurring as trace elements prove to be an even more sensitive probe for these conditions and processes. The need for sensitive micro-analytical techniques is particularly acute in experimental petrology, where the geological processes are simulated on a much smaller scale, and the resulting samples are microscopic.

In ore mineralogy trace element data can provide important indicators of the processes involved in ore formation and any subsequent diagenesis and metamorphism. For precious-metal ores, detailed mass balance calculations either for reserve estimation or evaluation of beneficiation efficiency often require the detailed distribution of the metal at trace levels carried by the constituent minerals [Cabri 1987].

Method

Proton microbeams are focussed primarily using quadrupole multiplets, but solenoids and plasma lenses are also used successfully. For quadrupole based lenses, magnetic systems predominate, and have produced the best resolution. The system at the CSIRO Heavy Ion Analytical Facility (HIAF) is an electrostatic "Russian quadruplet system" [Sie and Ryan, 1986, Sie et al, 1990a] and tests have shown that a 3 micrometre beam spot can be produced. While micrometre or even submicrometre resolution may be desirable in certain applications, in minerals research it must be weighed against other considerations:

- Quantitative analysis demands a low detection limit in an acceptable measurement time. At HIAF this minimum detection limit (MDL) is defined as $3.29 \sqrt{B}$, where B is the underlying background counts at the energy of the peak of interest over the range of 1.06 FWHM of the peak. This corresponds to 99% confidence limit for a standard deviation of $\sqrt{2}B$. Figure 1 (top) shows the MDL values for an assortment of minerals, for 10 microCoulomb beam charge and for a detector with 50 msr acceptance solid angle. A 2-3 ppm MDL of transition elements are obtained for a silicate matrix, e.g. garnet. The time

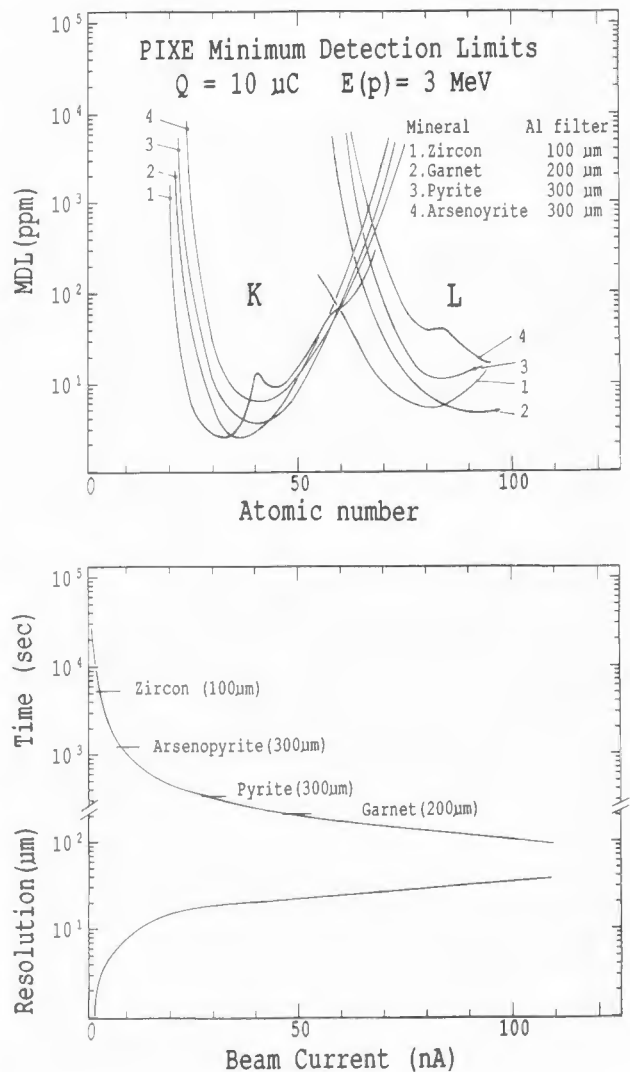


Figure 1. The top figure shows the minimum detection limits (MDL) defined at 99% confidence level for various elements in a number of minerals, detected either through their K lines or their L lines, for 3 MeV proton energy and 10 microCoulomb beam charge. The Si(Li) detector subtends a solid angle of 50 msr. The use of filters enhances the detection limit by suppressing the major element lines in the spectrum. Effects of the detector lineshape for high Z element can be seen in the case of zircon, where the detection limit in the vicinity of $Z = 40$ is worsened. The bottom figure shows the analysis time required. This depends on the beam intensity, which in turn is inversely related to the beam resolution. At high beam currents, the count rate in the detector defines the minimum time limit. The minimum times for the cases shown are given for a maximum count rate of 8000 counts per second.

required to accumulate the charge is given in the bottom Figure 1, as a function of the available beam

current. This in turn is determined by the beam resolution, also shown in the same figure. The 10 μC charge can be routinely achieved in 15 minutes using beams of 20 nA if a 15 μm beam is used. The measurement becomes impractical if the beam intensity falls below 1 nA. Proton sources are several orders of magnitude less bright than electron sources, and thus whereas nA's of beam is possible from electron microprobes at 1 micron resolution, for proton probes the intensity falls well below the 1 nA limit. The minimum time is defined either by the available beam or the count rate in the detector. If the count rate in the detector is maintained below 8000 counts per second, the minimum time required, corresponding to the maximum permissible beam intensity, is shown in Figure 1 (bottom) for a number of cases.

- The range of 2-4 MeV proton beam in minerals is $\sim 60 \mu\text{m}$ (in silicates, less in sulfides), but self-absorption effects of the X-rays in the matrix and the rapid fall of X-ray production rates with depth as the proton beam loses energy result in effective depths of analysis of $\sim 30\text{-}40 \mu\text{m}$. This has some bearing on the selection of samples to be analyzed: whenever possible grains size should not be less than $\sim 50 \mu\text{m}$ to avoid complications of contributions from the substrate or overlapping grains. Thus a beam spot of 5-30 μm in diameter is usually appropriate and provides ample scope for increased beam currents ($\sim 5\text{-}20 \text{ nA}$) necessary to achieve low detection limits. Samples are prepared exactly as required for electron microprobe analysis, although in view of the large effective depth of analysis of protons the surface finish requirement is not as stringent. On the other hand the specimen thickness should be thick enough to prevent excitation of the substrate.

In most PIXE applications, the X-rays are detected with an EDS (energy dispersive spectrometer) system, with Si(Li) being the most commonly used. Hyperpure Ge detectors are occasionally used to enhance detection of X-rays above 30 keV. Large volume Ge(Li) detectors are also used in conjunction with PIXE to detect gamma rays from selected light elements not detectable by PIXE. The use of WDS (wavelength dispersive spectrometer) systems are desirable, but at present their use is still not practical because of the limitations in the available beam current intensity.

The EDS offers convenience in enabling simultaneous multi-element detection, but also defines the regime of applicability. In typical measurements, filters are used both to protect the detector from the scattered proton beam, and more critically as a control of detector efficiency to enhance the sensitivity of detection of element(s) of interest. However, the thinnest absorber of the lightest element that can be used as filter (Be) virtually eliminates all X-rays below energies of $\sim 1 \text{ keV}$ defining the lightest element detectable to Na. For this reason, proton probe data must be complemented by electron probe data for the major elements. This can be conveniently used to normalize the

former when the accurate beam charge collection is not available.

In practice thicker filters are commonly used to attenuate the major element lines to permit higher beam currents to be used in order to enhance the detection of heavier trace elements, and to reduce pile-up effects that can interfere with the lines of interest (e.g. U and Rb can be masked by pileup from Fe). For the K lines, the upper limit is defined by the rapid decrease both in the proton ionization cross section for the K shell and in the efficiency of the Si(Li) detector above $\sim 30 \text{ keV}$, corresponding to Ba. From the lanthanides onward the L lines are used, but with the ubiquitous Fe K lines dominating most spectra, there is a gap in detection sensitivity from Ce to $\sim \text{Sm}$.

The detection sensitivity is affected by the continuum background, which for most minerals is mainly due to bremsstrahlung. The limited resolution of the Si(Li) and the response function itself, e.g. the low energy tail of the photopeak due to incomplete charge collection in the detector poses another source for degradation of the MDL. For instance, for high Z minerals such as zircon, the tail of the Zr peak presents additional background and thus reducing the sensitivity of detection of elements with X-ray lines below the Zr K lines, as can be seen in Figure 1. The dependence on the type of minerals is due to the differences in self absorption.

Many applications require analyses of large numbers of samples considering that geological samples commonly are variable in nature. The hardware and software must be designed to enable such operation. Desirable features include a facility for quick sample loading and the ability to view specimens readily with good magnification to both position the specimen at the beam spot location and to identify microscopic features. The ability to change filters quickly is another desirable feature, especially during reconnaissance studies of new types of specimens. The software must enable reliable analyses of many spectra with the least amount of intervention. One of the important features in the software developed at HIAF is the ability to treat layered targets as required for analysis of thin or buried samples, and the effects of secondary fluorescence [Reuter et al. 1975]. The spectrum fitting procedure incorporates a statistics-sensitive non-linear iterative peak-clipping (SNIP) algorithm which provides a reliable continuum background under low statistics peaks, both isolated and next to major lines [Ryan et al, 1988]. Up to triple pile up effects are also included in the spectrum fitting. The method is free of user adjustable parameters to permit batch processing, rapid and able to treat complex spectra [Ryan et al, 1990a]. Effects of matrix absorption on the relative intensities of suites of lines are precalculated. Up to 16 L lines and 9 K lines, including KLL and KMM radiative Auger lines are included in the calculation. The X-ray yields are based on the ECPSSR ionization cross sections theory of Brandt and Lapicki (1981) as calculated by Cohen and Harrigan (1985). The binary encounter approximation (BEA) theory [Garcia et al., 1973] for the ionization cross section are still used by many other workers and can be selected if required. The analytical

procedure has been tested against a number of geological standards for trace element analysis (BCR-1, AGV-1, GSP-1) and accuracies of 3% for major elements and down to 5% for trace elements depending on statistics have been demonstrated [Ryan et al, 1990b]. Details of the microprobe system at HIAF and the tests are described elsewhere [Sie and Ryan, 1986; Sie et al, 1989,1990a; Ryan et al 1990a, 1990b; Cousens et al. 1987a].

Applications

As anticipated from earlier applications of EMP, micro-PIXE has found an appropriate niche in igneous mineralogy and petrology. The earliest application of the proton microprobe was in fact the study of lunar and meteoritic material [Bosch et al, 1978, 1980] and this area continues to be a significant area of application [Blank et al, 1982,1984; Woolum et al. 1987, Bajt and Traxel 1991]. The distribution of incompatible elements, occurring as trace elements reveals detailed information about physico-chemical processes associated with the formation of these rocks. Similarly, in terrestrial samples the trace elements allow the study of geological processes such as magma mixing and evolution, and the geochemical composition of the upper mantle. Considerable new information on the upper mantle has been obtained from studies of xenoliths (fragments of lower crust or upper mantle rocks) and accessory mafic minerals in volcanic rocks of mantle origin such as kimberlites.

Collection by stream and soil sampling of these accessory minerals such as Cr-pyrope garnets ($(\text{Mg,Fe})_3(\text{Al,Cr})_2(\text{SiO}_4)_3$), chromian spinels ($(\text{Fe,Mg})(\text{Cr,Al})_2\text{O}_4$) and ilmenites ($(\text{Fe,Mg})\text{TiO}_3$) has been the basis of diamond exploration, as a means of finding diamondiferous kimberlites [Griffin et al, 1990]. These minerals are dispersed by but resistant to weathering and their characteristics are used as means to find the source rock itself, and to assess its prospectivity. One of the aims of the micro-PIXE study of these indicator minerals is to investigate the possibility of identifying the type of source rocks and multiple sources [Griffin et al, 1990]. Chromites for instance, are frequently used being most resistant to weathering, but can originate from various types of barren igneous rocks as well as from kimberlites. Figure 2 shows the trace element content of chromian spinels showing grouping of samples from different types of rocks. These trends, and those from accompanying trace elements, can be used as the basis of a quantitative classification schemes.

Figure 3 shows the distribution of trace elements in ilmenites from a number of kimberlite pipes in South Africa, showing the grouping according to source. The grouping reflects the magmatic products sampled by the kimberlite, whereas the variation within each group reflects the effects of fractional crystallization. As such magmas cool, they precipitate various minerals which deplete or enrich the magma in certain elements: precipitation of mafic silicates such as olivine ($(\text{Mg,Fe})\text{SiO}_4$) depletes the magma in Ni and that of zircon (ZrSiO_4) in Zr, while the incompatible

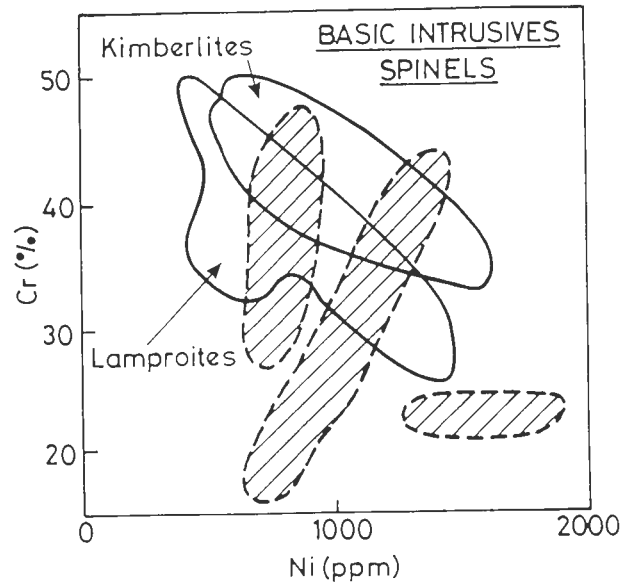


Figure 2. Correlation diagram of the distribution of trace element Ni plotted against the major element Cr from chromites (Cr-spinel) show grouping according to the source rock types. The shaded groups belonging to various barren igneous rocks (gabbros, greenstone) show different trend to kimberlites and lamproites, the two types of rocks which can be diamondiferous [from Sie et al 1989, Griffin et al 1990].

element Nb is steadily enriched in the residual magma and its products.

While partitioning of elements between the melt and the crystallizing phases is already useful as an empirical, qualitative guide for exploration purposes, it is even more exciting to use it quantitatively in modelling the evolution of magmas. The partition coefficients, sensitive to the composition of the parent magma(s), pressure (P) and temperature (T) and valence of the elements can be derived from natural systems if they are known to be closed and in equilibrium. Alternatively they can be obtained experimentally from systems created in the laboratory which simulate mantle conditions. Micro-PIXE applications in experimental petrology offer the prospect of systematic studies of partitioning of geochemical marker elements, such as the HFSE (high field strength elements - e.g. Zr,Nb,Ta), the LILE (large ion lithophile elements - e.g. Rb,Ba,Sr,Y) groups and possibly some of the REE (rare-earth elements) between coexisting phases and for different types of magma under various conditions. For most of the minerals of interest (e.g. garnet, pyroxenes, olivine and amphiboles) MDL values of around 2 ppm can be obtained readily (in 4 - 10 minutes with a 5-15 μm beam for a collected charge of 3 μC) for the LILE and HFSE groups, but for all but the heaviest REE the detection limit is poor at around 50-200 ppm because of the limitations discussed above.

One experimental study of partitioning of Nb and Ta between basaltic melt and the crystallizing phases has

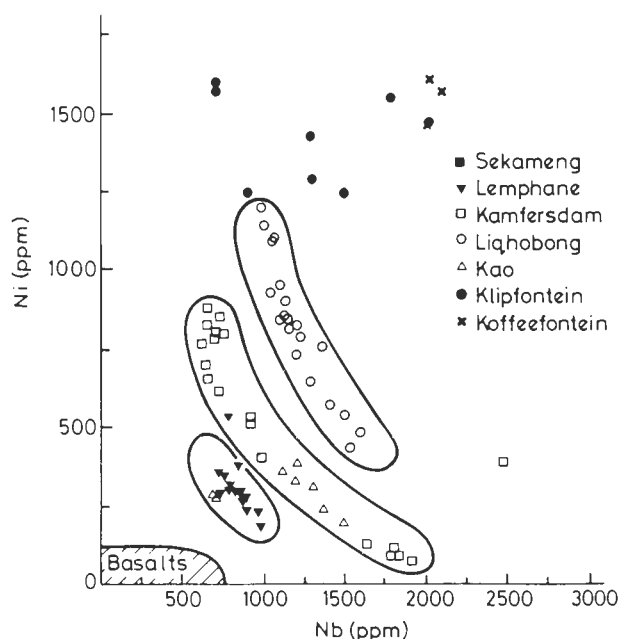


Figure 3. Distribution of trace elements Ni, Nb in ilmenites from various kimberlite pipes show groupings which can be used to identify multiple sources. The grouping represents the variation in the parent magma, while the trend in the group reflects the effects of fractional crystallization during the cooling of the magma. The distribution from kimberlites are well separated from that obtained from barren basalt (left). The fractional crystallization effect can be followed in detail in one pipe. Precipitation of olivine depletes the melt in Ni, and zircon in Zr, while the element Nb is steadily enriched in the residual magma and its product [from Sie et al 1989, Griffin et al 1990].

suggested large fractionation effects in the partitioning of Nb and Ta, hitherto assumed to be geochemically coherent [Green et al. 1989]. Similarly, in systems of mixed, or immiscible melts (e.g. carbonatite and silicic melts), the presence of volatiles and fluids can now be studied at levels close to natural systems. A recent experimental study [T.H. Green, S.H. Sie to be published] of partitioning of these elements in a mixed silicate and carbonatite melt confirmed in detail the preference of LILE to partition into carbonatites.

The pressure and temperature dependence of the partitioning of elements between coexisting phases, usually pairs of minerals, has been exploited as the basis of geothermobarometry. Examples are the orthopyroxene/garnet barometer and the two-pyroxenes [Finnerty and Boyd (1987)], or garnet/olivine [O'Neill & Wood (1979, 1980)] thermometers. One of the most exciting results of the indicator-mineral study is the discovery of a single mineral thermometer: the Ni thermometer [Griffin et al, 1989]. This is based on the strong temperature dependence of the partitioning of Ni between garnet and olivine. However the Ni content of olivine is relatively constant over a wide range of temperature, thus allowing the use of the garnet alone.

The single mineral thermometer has significant implications in diamond exploration, where the coexisting mineral is not usually available. Diamonds are formed in a broad range of high pressure and temperature within the diamond stability field. In craton areas, the geotherm intersects this field between 900-1200°C. Analysis of the Ni in garnets can be used to assess whether the host rock sampled material from depths conducive to diamond formation [Griffin et al 1990].

During crystallization of minerals, fragments of other crystals present or portions of the melt or fluid can be trapped in the crystal to form inclusions. Isolated from further evolution, these inclusions preserve information about P,T and chemical features of the system at the moment of trapping. Micro-PIXE is ideally suited to study these inclusions, which are typically minute (few tens of μm or smaller).

Diamonds often contain such inclusions, classified according to two major mantle rock types: peridotitic (olivine and Cr rich garnets and spinels) and eclogitic (mainly clinopyroxene and low Cr garnets) suites. In one study of West Australian diamonds, evidence of disequilibrium based on the trace element compositions of the inclusions led to the conclusion that the diamonds grew in an open system [Griffin et al, 1988a].

Melt inclusions trapped in mantle minerals, e.g. olivine, present the opportunity to study the geochemistry of the mantle. While the heterogeneity of the mantle is widely accepted, direct evidence from the compositions of mantle xenoliths and so-called primitive magmas (high Mg content) is complicated by various processes, e.g. magma mixing, crustal assimilation, fractional crystallization and metasomatic events prior to the eruptive emplacement. Ratios of trace elements of the HFSE and LILE groups in melts are known to be distinctive in different tectonic environments [Pearce and Cann, 1973] and thus the study of their content in these inclusions can reveal the characteristics of the primitive or source mantle magma. A micro-PIXE study of inclusions from several tectonic environments and lunar material [A.V. Sobolev, S.H. Sie, to be published] shows that these ratios (e.g. Zr/Y, Sr/Y) could be very different from the host rock, and cannot be explained by fractional crystallization effects of other phases present. This indicates magma mixing and other processes during the evolution of the magma, while the characteristics of the mantle source are preserved in the inclusion. Figure 4 shows spectra obtained from inclusions from three tectonic settings: continental lithosphere, mid ocean rift and subduction zones. The contrast in the Zr/Y ratios are evident from the raw spectra after allowing for overlaps of the K alpha and K beta lines of the suite of elements (Rb,Sr,Y,Zr,Nb). The overlaps are resolved in the fit to the spectra, and the extracted Zr/Y ratios are 21, 5 and 1 respectively for the three cases shown. The Ni observed in the spectra originate from the host olivine and was used to estimate the thickness of the inclusion samples. Figure 5 illustrates the method to estimate the uncertainty in the deduced concentrations of these elements using the Ni content as a guide. The yield of these elements normalized to the Fe content as % of that

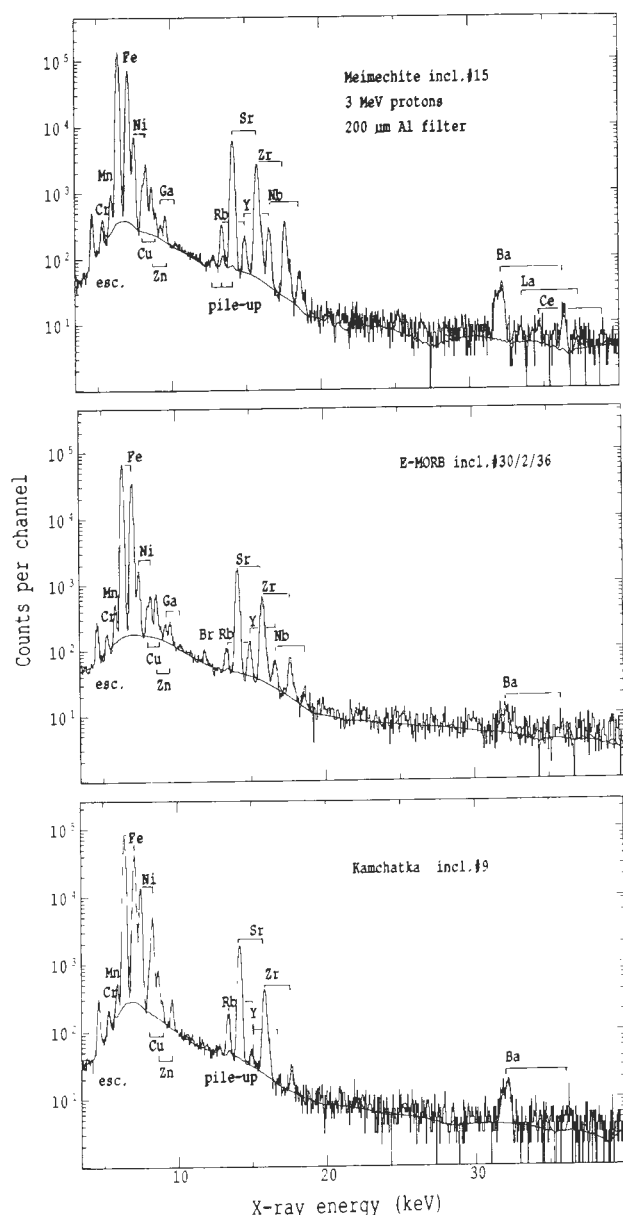


Figure 4. Spectra from melt inclusions in olivine from ultramafic rocks from different tectonic settings: continental lithosphere (top), mid-ocean rifts (middle) and subducted zone (bottom). The trace elements of interest are Rb, Sr, Y, Nb, Zr, Ba which are completely incompatible with olivine. The Ni observed in the spectrum is due to the olivine and is used to estimate the olivine contribution to the spectrum. The ratios of these elements to the Y content however should be unaffected and as can be seen vary widely with the different tectonic setting.

from an infinitely thick sample is plotted against the corresponding ratio for Ni normalized to the measured Ni content of the olivine. The olivine could also be analyzed if the beam drifts away from the sample during the analysis.

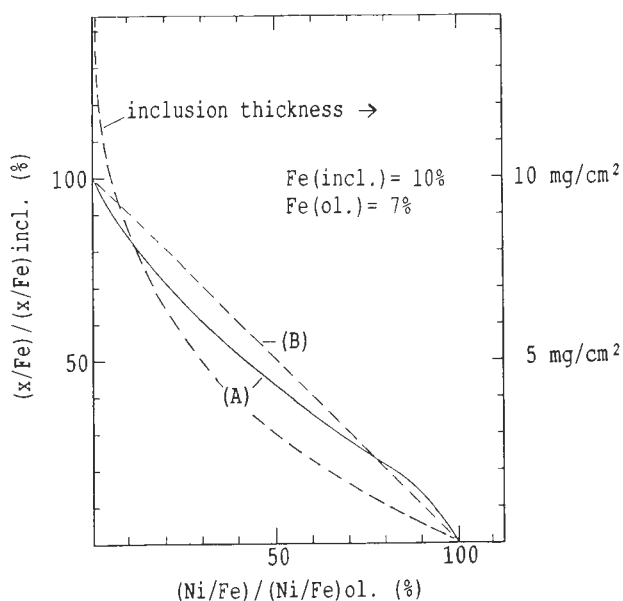


Figure 5. The Ni in the spectrum in fig. 4 is assumed to be due entirely to olivine, and thus can be used to correct the data. Theoretical calculation of the yield of elements X normalized to the Fe content as % of that from an infinitely thick sample is plotted against the corresponding ratio for Ni normalized to the measured Ni content of the olivine. The curves are calculated for Zr but the results for the other elements Rb, Sr, Y, Nb and Ba are the same within 1%. The two curves shown are calculated for the two extreme cases: the samples are infinitely wide and hence the Ni can only come from the underlying olivine, and in alternatively the olivine due to the drift of the beam during analysis. The two curves give the maximum uncertainty in the absolute concentration for a given Ni content in the spectrum, which are of the order of 10%.

The two curves shown are calculated for the two extreme cases: the samples are infinitely wide and hence the Ni can only come from the underlying olivine, and in alternatively the olivine comes only from the beam drift. The two curves give the maximum uncertainty in the absolute concentration for a given Ni content in the spectrum, which are of the order of 10%. However, the elements Rb, Ba, Sr, Nb, Zr and Y are totally incompatible with olivine so the ratios should not be affected by olivine contamination and can be used reliably. The study shows a wide range in the distribution of ratios, depending on the tectonic setting, and that the LILE/Y ratios are generally correlated with Zr/Y ratios except for Sr/Y which is affected by the presence of plagioclase [A. Sobolev et al, to be published].

Evidence of alteration processes in the mantle is found in metasomatized xenoliths, not only in the composition, but also in the microstructure of minerals. Smith and Boyd [1987, 1989] explained the zoning profiles on garnets in sheared xenoliths from the kimberlites in southern Africa as evidence of infiltration by melts/fluids prior to eruption.

Micro-PIXE studies [Griffin et al, 1988b, Smith et al, 1991] of similar samples revealed corresponding zoning of some of the trace elements which provided further clues on the nature of the infiltrating fluid and on the time scale of both heating and infiltration. Interpretation of the evidence of metasomatism found in both deformed and undeformed xenoliths is still a controversial subject. In the xenolith from the Frank Smith mine example [Griffin et al, 1988b], the clinopyroxene does not show zoning, indicative of high diffusion coefficients and rapid homogenization, whereas in another study, the clinopyroxene in metasomatized spinel lherzolite xenoliths shows evidence of zoning [Greig et al, to be published]. What is understood is that it is a complex process of both physical and chemical alteration of wall rocks in contact with magma or fluids, which can themselves be undergoing differentiation [O'Reilly and Griffin, 1988]. Whether the same agent causing obvious ("patent") chemical changes, e.g. the presence of hydrous secondary minerals, is also responsible for the more subtle ("cryptic") changes observed (e.g. the zoning profiles and enrichment or depletion of trace elements), is not conclusive and the problem remains an exciting area of application of micro-PIXE.

Minerals formed in hydrothermal systems contain fluid inclusions, relics of the mineralizing fluids. In addition to the homogenization temperature, the composition of the fluid inclusion reveals the characteristics of the mineralizing fluid. While occasionally there can be large (millimeter size or greater) fluid inclusions, more often they are minute with dimensions in the tens of microns or less. Bulk techniques involving crushing and leaching have been used to determine the average composition, but in this method different generations of inclusions are scrambled together. Microanalytical methods such as ion-microprobes, electron microprobes and laser ablation have been used to infer the composition, but these involve decrepitation of inclusions. This may result in partial or complete loss of elements carried by volatile components. Exploiting the large penetration depths of the proton beam (e.g. about 60 μm in quartz) it is possible to study these inclusions without decrepitation [Horn and Traxel 1987, MacArthur et al. 1990, Ryan et al. 1991]. At HIAF, the inclusions to be studied are judiciously selected to be as near to the surface as possible (5-15 μm) for efficient production of the X-rays of interest from the inclusion and minimizing contribution from the host minerals, but allowing sufficient depth from the surface to avoid rupture under beam bombardment. A typical spectrum obtained from a fluid inclusion is shown in Figure 6. In this case, the ratio of the Cl K_{α} to K_{β} ratio is used to determine the depth of the inclusion to an accuracy of ~ 1.6 μm [Ryan et al, 1991]. The uncertainty in estimation of the depth and the usually irregular shape of the inclusion are the limiting error. However, it is possible to obtain reliable results when appropriate corrections are applied [Ryan et al, 1991].

Precious metals (Ag, Au and PGE-platinum group elements) are often carried at trace levels by sulfides either in solid solution or as sub-microscopic inclusions. However

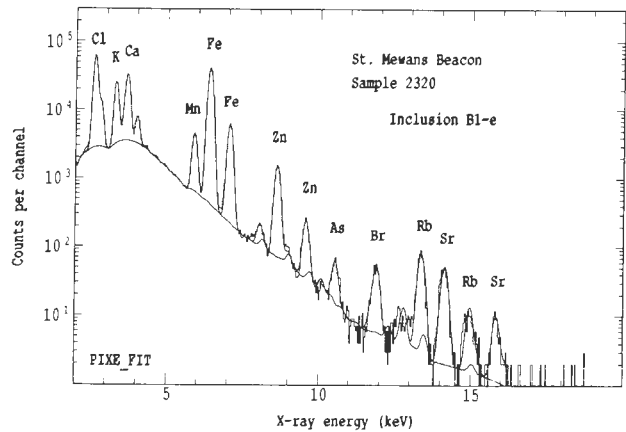


Figure 6. A typical spectrum from analysis of a fluid inclusion in quartz at about 13 μm depth below the surface. The depth is estimated from the Cl K_{α}/K_{β} ratio to an accuracy of ~ 1.6 microns [from Ryan et al, 1991].

other trace elements in sulfides (Cd, Sb, Sn, In, Se, Te) are also of interest from the ore genesis point of view.

Micro-PIXE has been used to determine Ag and other trace element distribution both in ore samples [Cabri et al 1984, 1985; Harris et al 1984, Reeson et al 1990] and in mill concentrates [Sie et al, 1989]. While galena (PbS) is a common carrier of Ag, other phases e.g. chalcopyrite (CuFeS_2) can also be significant carriers. Considering the large quantities of ores processed in base metal smelting, recovery of trace quantities of Ag both in tailings and the main concentrate can translate into substantial additional revenue. With detailed distribution of Ag known, mass balance calculations can be carried out to evaluate the efficiency of the beneficiation process. In galena, sphalerite (ZnS) and chalcopyrite the MDL of Ag is typically ~ 10 ppm.

Similar analysis can also be applied to determine Au distribution, particularly in refractory Au ore, so-called because of its resistance to conventional cyanidation process. The unliberated Au is usually locked in solid solution in various phases, with arsenopyrite (FeAsS) being the most common carrier. However other more abundant phases, e.g. pyrite (FeS_2) and pyrrhotite (FeS) can also carry some of the Au. An MDL of 5 ppm can be achieved in pyrite and pyrrhotite, while in arsenopyrite a poorer sensitivity at 40 ppm is caused by the effect of the "tail" of the As K_{α} line that increases the background level for the Au L_{α} line [Sie et al, 1989]. By using ion implanted standards [Chryssoulis 1989, Chryssoulis et al 1989] for accurate quantification, Cabri et al [1991] have demonstrated that ion microprobe analysis can be used effectively in Au determination in arsenian pyrite. Practical MDL values of ~ 0.4 ppm were obtained, which were compared with 20-26 ppm by micro-PIXE for about twice the analysis time of about 15 minutes. While the ion microprobe has better detection limit, the micro-PIXE can be applied more readily without the need for elaborate standardization. In the example cited (Cabri et al, 1991) the resultant errors of

7-10 ppm in the ion microprobe measurements due to uncertainties in implant dose, depth measurements, counting statistics and density inhomogeneity are comparable to the micro-PIXE errors of 11-26 ppm for the same set of samples. The synchrotron radiation probe has also been used to determine Au with an MDL of 0.8-3 ppm [Chen et al. 1987] and spatial resolution of 20x20 μm . However the typically limited access to such a facility may preclude its use as a routine technique.

As in the case of Au, the detailed distribution of PGE (platinum group elements: Pt, Pd, Rh, Ir, Ru, Re, Os) in an ore is of interest because of their high monetary value. While most PGE occur as free PGM (platinum group minerals) readily separable, economic quantities may be carried in other phases. A micro-PIXE study of the Merensky Reef ore revealed pentlandite ((Fe,Ni)₉S₈) as a significant carrier of Ru, Rh, Pd at levels up to few hundred ppm, and to a lesser extent pyrrhotite as carrier of Ru (8-12 ppm) [Cousens et al, 1987b, Sie et al 1990b]. In these minerals typical MDL values are 2-6 ppm. Orberger and Traxel (1991) measured Pd and Se content of Ni-Cu mineralization in an ophiolite complex, and also found that Pd is carried mainly by pentlandite. Similar results have been obtained from ore samples from the Stillwater and Sudbury complex [Cabri et al 1984].

Other trace elements can contain genetic information, although at present the data are often difficult to interpret. Frequent associations of As with Au, e.g. the fact that arsenopyrite and arsenian pyrite are often carriers of Au lead to the anticipation that a genetic relationship can be found, especially in epithermal systems. A detailed study of the trace element distribution in pyrite in an epithermal system [Griffith et al, 1991] revealed a broad spatial correlation of Cu, Sb, Se with As, and with Ag-Au grades, but there was no recognizable systematic variation in the chemistry of the pyrite near the mineralized zones. This was attributed to the fact that the pyrite formation occurred over more episodes than the precious metal deposition.

The trace element distribution in gold itself may be a better discriminant for genetic associations. The level of Ag which is nearly universally present and alloyed in Au is related to temperature of formation and salinity of the mineralizing fluid. Other trace elements in Au (Fe, Cu, Zn, Hg, Pb) were originally detected by spectrographic techniques by Warren and Thomson [1944], who went on to conclude that their variation are controlled by the characteristics of the metallogenic provinces rather than the type of deposit. Micro-PIXE enables systematic non-destructive study of detrital Au to test this hypothesis, which if proven generally would have significant implications in exploration. A preliminary study on bedrock and alluvial Au grains from several prospects in Tasmania appears promising in showing differences in the trace element distribution between different deposit types and styles of mineralization, between deposits of the same type and between different mineralogical associations [Sie et al, 1991]. Analysis of gold grains highlights the limits of the EDS system: most elements adjacently below Au are virtually undetectable at

levels below 0.1%. The elements immediately above Au (Hg, Pb, Bi) can be detected through their L_{γ} lines with MDL values of ~200 ppm.

Conclusion

The present applications are based mainly on EDS systems, which define most of the limitations and the principal advantage of multi-element detection. Detection of REE is still not satisfactory, nor are detection limits for samples where the major element is of high Z, e.g. zircons, Au grains, galena. The use of WDS is desirable but at present it is precluded mainly because of the limitations of the proton microbeam intensities.

On the physics side there is still the unresolved question on the accuracy of the calculated cross sections for X-ray production. There is a systematic difference in the energy and Z dependence of the ionization cross section between the ECPSSR theory and the BEA theory used by many other PIXE users. However some of this problem can be circumvented through calibration against standards.

For large scale applications, appropriate for routine applications in exploration programs, it is desirable to reduce the unit cost of analysis. This can be achieved for instance by employing multiple detectors, which may be possible for a specific situation but difficult or expensive to implement for a more versatile system.

Despite the clear advantage of micro-PIXE in many areas, one has to be continually aware of alternative methods which can be more viable in specific cases, for example the use of SIMS for detection of Au in sulfides. The synchrotron radiation probe is also an alternative, and as more facilities become available routine applications may become possible, and competitive with micro-PIXE especially in the REE detection. Accelerator mass spectrometry is another new technique that can be used with sub-ppm detection limits for heavy elements, but further development is required to improve the spatial resolution of the sputtering beam which currently stands at ~0.5 mm [Rucklidge et al, 1990].

The examples presented above clearly demonstrated the versatility of micro-PIXE in the geosciences and minerals research. Most applications can be regarded as an extension of EMP methods, but the higher sensitivity of PIXE reveals new features otherwise difficult to obtain or not obtainable at all non-destructively. The larger range of protons used in the analysis allows new types of measurements to be carried out (e.g. fluid inclusions). Real progress is marked by the transition from experimentation stage to contribution to the mainstream of geoscience, as for example in igneous petrology.

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Discussion with reviewers

G.Remond: You refer to the work by Chrysosoulis et al., using ion implanted mineral for the analysis of Au with SIMS. Did you try to use implanted materials for calibrating your analytical procedure?

Authors: There is no advantage in using implanted standards for PIXE because the uncertainty in the depth profile of the implanted element(s) will contribute to errors even when the exact dosage is known. Homogeneously doped standards would be preferred although they are not any easier to prepare. In SIMS an implanted standard is needed to normalize the sputtering yield of the element of interest, which is dependent not only on the matrix but also on the conditions during the measurement.

M.L.Rivers: What are the problems associated with radiation damage in micro-PIXE?

Authors: Most minerals, especially igneous ones are stable under beam bombardment, but thermal damage can occur at high currents resulting in fractures. Thermal effects will result in loss of material in hydrous minerals and carbonates. In such cases one should reduce the beam intensity, or reduce the beam areal density by defocussing the beam. This is usually investigated during reconnaissance runs. More often the problem is the failure of the epoxy employed to hold the mineral grains, resulting in loss of the specimens.

M.L.Rivers: What are the costs (capital and manpower) involved in setting up a micro-PIXE facility?

Authors: A micro-PIXE facility can be built around a dedicated accelerator, e.g. a 1.7 MV tandem or 3 MV single ended electrostatic accelerator. This can cost anywhere between \$400K to \$1M. The microprobe system can be built for around \$300K and anywhere between \$40-200K for the data acquisition and analysis computers, depending on the degree of sophistication and application requirements. A minimum of 3 man-year scientific plus 3 man-year technical support would be required to put it all together. These figures are based on our experience in commissioning HIAF. With the present availability of suppliers of lenses and software packages, I believe that a basic, turn-key system can be built for around \$1.2M.

K.Traxel: You mention that spatial resolution is of secondary importance in geochemical applications. Using the partitioning of trace elements between coexisting phases as a geothermometer must, however, also take care of the possible zoning of the trace elements, especially in experimental petrology with its microscopic grains. Do you agree that spatial resolution is important in this context?

Authors: I agree that the spatial resolution is a desirable feature, but one must be aware of the consequence of the relatively large (10-30 μm) effective depth of analysis in PIXE. If the zoning features are say less than 2 μm , then the

specimen will have to be prepared as a thin section of comparable thickness; otherwise the analysis will inevitably average over several zones. The ultimate limitation would be the beam intensity: with the presently available proton sources the best beam current at 1 μm resolution is only 100 pA. It would be impractical from measurement time consideration to carry out many spot analyses at beam current levels less than 1 nA.

K.Traxel: Diamond is an ideal matrix for the proton microprobe. Do you think that investigation of inclusions could help in optimizing the production process for artificial diamonds?

Authors: The diamond inclusions reveal the conditions of diamond growth in natural geological systems, which are generally more complex than can be simulated under laboratory conditions. The phase diagram (graphite-diamond) however is predominantly determined by P and T, and thus in principle it would be easier to produce diamonds artificially than to understand the exact conditions of diamond production in nature.

S.Tapper: How are the detection limits in microbeam PIXE compared with the electron microprobe using a WDS detection system in the region where L lines are used?

Authors: Detection limits by definition depend on conditions of measurements, and in many cases the type of matrix and interferences. Under favourable conditions WDS with EMP can achieve 100 ppm MDL for heavy elements (rare earth elements and heavier) using the L lines, and sometimes better (50 ppm) if M lines are used. In PIXE with an EDS the presence of Fe (typical for geological samples) limits the use of L lines to elements heavier than Sm, and typical detection limits are between 10-100 ppm for integrated beam charge of 3 μC . For beam spot sizes of not less than 10 μm this can be achieved in 4-15 minutes, with the shortest counting time limited by the count rate in the detector. It should be noted that EDS is a multi-element detection, and that WDS measurements typically require 3-4 minutes per element.

S.Tapper: Is there enough difference between the matrix of the fluid inclusion and the surrounding mineral, to enable a (simultaneous) RBS analysis measurement of the depth of the inclusion?

Authors: Tests that we have performed using combined RBS and PIXE on fluid inclusions in quartz were not encouraging. The already small contrast in energy between protons scattered from the fluid-quartz interfaces are further obscured by the structure in the distinctly non-Rutherford cross section of scattering on Si, O and C present in the fluid.

The first part of the document discusses the importance of maintaining accurate records of all transactions. It emphasizes that every entry, no matter how small, should be recorded to ensure the integrity of the financial statements. This includes not only sales and purchases but also expenses and income. The document also highlights the need for regular reconciliation of bank statements and the company's records to identify any discrepancies early on.

In addition, the document provides a detailed breakdown of the accounting cycle, from identifying the accounting entity to preparing financial statements. It explains how each step contributes to the overall accuracy and reliability of the financial data. The document also includes a section on the classification of assets and liabilities, providing examples and explanations for each category.

The second part of the document focuses on the practical application of these principles. It includes a series of exercises designed to help students understand how to record and classify transactions. These exercises cover a wide range of scenarios, from simple sales and purchases to more complex transactions involving multiple parties and accounts. The document also includes a section on the preparation of financial statements, showing how the data from the accounting cycle is used to create the balance sheet, income statement, and statement of cash flows.

Finally, the document concludes with a summary of the key points discussed and a list of references for further study. It emphasizes that a strong understanding of accounting principles is essential for anyone involved in the financial management of a business. The document also includes a glossary of key terms and a list of additional resources for students who want to learn more about accounting.