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D. Allan Bromley: Referrals [2 of 7] [1992]

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ORIGINATOR: 02

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DIRECTORATE STATUS

FROM: SIE, Soey: CSIRO AUSTRALIA

TO: DR. D.A. BROMLEY

DATE OF
CORRESPONDENCE: 12/07/92

SUBJECT: HE IS WRITING WITH PERSONAL INFORMATION AND
REQUESTING A RECOMMENDATION FROM DR. BROMLEY.

DIRECTORATE

STAFF

ASSIGNED: D. Allan Bromley

ASSIGNED:

ACTION

STAFF

REQUIRED: AS NECESSARY

ACTION:

SENDER'S DUE DATE:

OSTP DUE DATE: 12/30/92

STAFF DUE DATE

DATE COMPLETED:

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CENTRAL FILES:

Withdrawal/Redaction Sheet

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Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
01a. Letter	To: Allan Bromley From: Soey Hian Sie Re: Request for recommendation [personal information redacted] (2 pp.)	12/7/92	(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
Re-review Case #:		Appeal Disposition:	
P-2/P-5 Review Case #:		Disposition Date:	
AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

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Withdrawal/Redaction Sheet

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Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
01b. Resume	Resume of Soey Hian Sie [personal information redacted] (1 pp.)	11/92	(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
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AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

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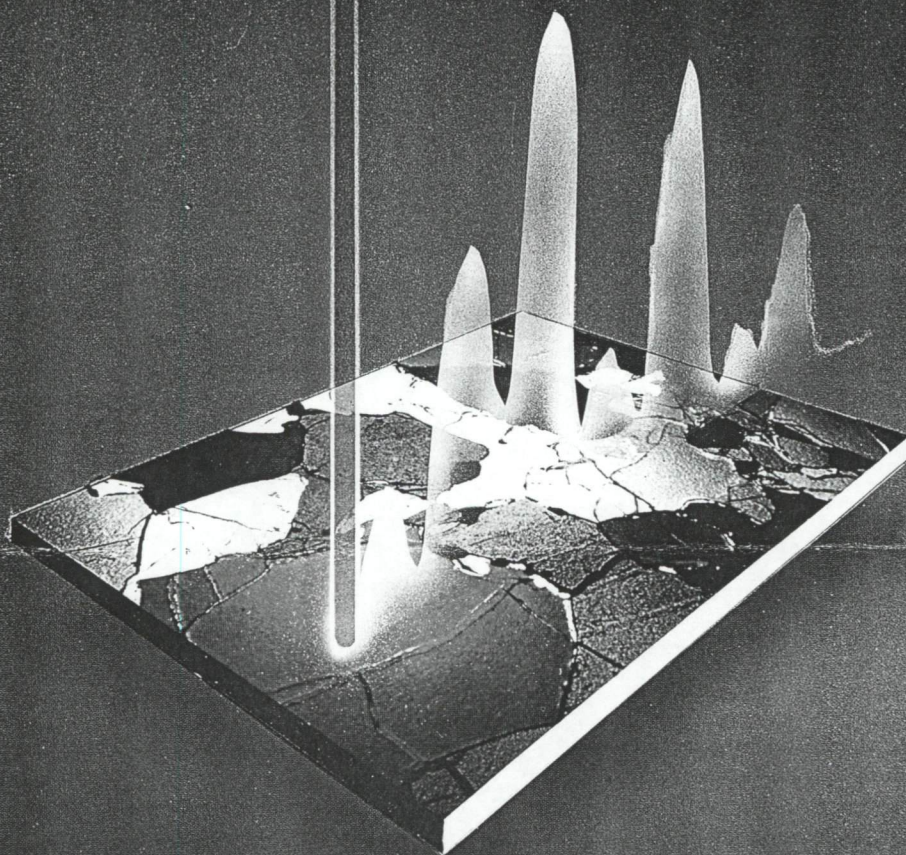
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D I V I S I O N O F

MR 85 17

DEPTH PROFILES OF HYDROGEN AND OXYGEN IN HYDROGENATED AMORPHOUS SILICON THIN FILMS

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Detailed depth profiles of hydrogen and oxygen have been measured in samples of thin films of a-Si:H produced by dc magnetron glow discharge techniques. The resonant capture reaction $^1\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}$ at $E_{^{19}\text{F}} = 6.417$ MeV was used for hydrogen profile measurements, and resonant α scattering at $E_\alpha = 3.0359$ MeV was used for oxygen. Contrasting results reflecting the different fabrication conditions were obtained and these were correlated with measured electrical properties.

1. Introduction

The electrical and optical properties of a-Si:H produced by glow discharge decomposition of silane are related to the distribution of hydrogen. Incorporated in the silicon network, hydrogen increases dopability by terminating dangling bonds [1]. However hydrogen may also be present in other forms, particularly as hydroxyls when moisture absorption occurs, which could be detrimental to the electrical properties.

The presence of oxygen in the bulk of a semiconductor can also affect its electrical properties, and on the surface it can affect contact properties, which are important for device applications. Surface defects may in fact dominate electrical properties by creating mobile carrier accumulation layers [2]. Oxidation can be expected to be one source of oxygen, but a major contribution could come from adsorption and absorption of moisture into microvoids, typically found in films of semiconductor produced by vacuum deposition techniques. The porosity of the films depends on the fabrication conditions, and thus the hydrogen and oxygen contents may be used to diagnose the effects of different conditions.

In the following, a number of samples of thin films of a-Si:H produced by dc magnetron glow discharge have been studied. Hydrogen profiles were determined using the $^1\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}$ resonant reaction at a ^{19}F bombarding energy of 6.417 MeV. Preliminary results of these measurements have been reported [3].

Oxygen content is usually determined as part of the hydroxyl using the infrared absorption (IR) technique [4], which does not provide depth profile information. Some attempts have been made to measure oxygen profiles using Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS), but quantita-

tative interpretation of the resultant data is difficult [5]. Electron energy loss spectroscopy (EELS) and Rutherford back scattering spectrometry (RBS) can yield information on depth profiles, but the nuclear reactions $^{18}\text{O}(p, \alpha)^{15}\text{N}$ and $^{18}\text{O}(p, \gamma)^{19}\text{F}$ are more commonly used [6]. These reactions however rely on the rare isotope ^{18}O , and are therefore impractical due to the reduced sensitivity in natural targets. The deuteron reactions $^{16}\text{O}(d, p)$ or (d, n) have also been used, but the high radiation background produced by these beams makes the technique less attractive [6].

In this paper, we report the use of resonant α scattering to determine the oxygen profiles, exploiting the resonance at an α bombarding energy of $E_\alpha = 3.0359$ MeV. Results are presented together with hydrogen profiles obtained from the same specimens, to delineate the sources of these elements and correlate them with the properties of the samples.

2. Experimental procedure

2.1. Film preparation

Various parameters in the glow discharge deposition of a-Si:H in the dc magnetron system have a considerable impact on the electrical, optical and mechanical properties of the films [7]. In particular, very significant differences are observed between samples prepared with the substrate at cathode potential, where there is considerable bombardment by energetic positive ions and also fast deposition rates of up to 3.5 nm/s. Electrical measurements have indicated that the surfaces play a more significant role under these conditions, and one aim of this study was to see whether the hydrogen and oxygen profiles could be used to distinguish between

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ANALYSIS OF CARBON CONTENT AND DISTRIBUTION IN $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ FILMS BY RESONANT SCATTERINGS.H. SIE¹⁾, D.R. McKENZIE²⁾, G.B. SMITH³⁾ and C.G. RYAN¹⁾¹⁾ CSIRO Division of Mineral Physics, PO Box 136, North Ryde, NSW, 2113, Australia²⁾ School of Physics, University of Sydney, Sydney, NSW, 2006, Australia³⁾ Department of Physics, New South Wales Institute of Technology, Sydney, NSW, 2007, Australia

Resonant alpha scattering has been used to determine detailed depth profiles of carbon in amorphous silicon carbon alloys produced by glow discharge decomposition. The carbon profiles exhibit a two layer structure similar to that indicated by hydrogen profiles in $a\text{-Si:H}$ films. By comparison electron probe analysis seems to considerably overestimate average carbon content while electron energy loss measurements on very thin specimens agree with the surface layer content in the resonance profiles of thicker films. The bulk content is, however, still lower.

1. Introduction

Amorphous hydrogenated silicon–carbon alloys have important applications in optoelectronic devices. They have a variable optical gap [1] according to the carbon content, adjustable from 1.8 eV for $a\text{-Si:H}$ through a maximum value of around 2.4 eV for intermediate compositions to 2.0 eV for $a\text{-C:H}$. The alloys can be produced by glow discharge decomposition techniques from mixtures of silane and methane. The rates of decomposition of the two gases vary with conditions of manufacture and the mixture, and thus the carbon content of the resultant material must be determined independently.

Unfortunately, although there are a number of studies of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ in the literature, most of the methods used for the analysis of film composition are dubious. It has recently been found [2] that two methods of analysis, electron probe microanalysis (EPMA) and electron energy loss spectroscopy (EELS) give results differing by as much as factor of 2. Conventional RBS (Rutherford backscattering) methods could, in favourable cases (e.g. for thick films $> 1\text{ }\mu\text{m}$), be used to determine C content, but detailed profiles cannot be determined reliably by this method. However, a strong resonance occurs at a higher bombarding energy $E_\alpha = 4.26\text{ MeV}$, which enhances the detection sensitivity and, as a result of its narrow width, enables measurements of detailed depth profiles [3].

In the following, carbon profiles in several $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ thin film samples produced by the dc magnetron glow discharge method were obtained using the resonant α scattering technique. The results are compared with other methods. The oxygen contents of some

of the samples were also examined by the resonance scattering method [4].

2. Experimental method

2.1. Sample preparation

The dc magnetron apparatus used in the production of the specimens has been described in detail elsewhere [5]. The cathode was stainless steel which was operated in a condition in which it became overcoated with silicon and carbon. Various mixtures of semiconductor grade silane (SiH_4) and ultra high purity methane (CH_4) gases were used. Operating conditions for the magnetron are shown in table 1. Substrates for the specimens were mounted on the anode. The cathode was operated for 5 min in the gases to be used for deposition before the sample was inserted. Various substrate temperatures were used, in the range $26\text{--}500^\circ\text{C}$ (table 2). Film thicknesses were measured using a Talystep step height gauge.

Table 1
The deposition conditions for $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films

Discharge voltage	900 V
Current	30–50 mA
Magnetic field	0.01 T
Total gas pressure	1.2 Pa
Substrate (anode) cathode distance	30 mm
Substrate temperature	25–500°C

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

KEY WORDS: Proton-microprobe, PIXE, X-ray analysis, trace element, geology, mineralogy.

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An AMS facility for minerals exploration research

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An AMS (accelerator mass spectrometry) system based on a Tandetron has been constructed at the CSIRO HIAF laboratory at North Ryde, and is currently undergoing tests. The system is designed to enable cosmogenic isotope based chronology, and eventually will be developed to enable ultratrace measurements in mineralogical samples.

1. Introduction

HIAF is an analytical laboratory based on a model 1430 Tandetron accelerator, commissioned in late 1983 [1]. It is dedicated to developing IBA (ion beam analysis) and AMS applications in the geosciences in support of the Australian minerals industry. An essential requirement for mineralogical and petrological applications of IBA is the development of the proton microprobe, completed in 1985, to enable in situ microanalysis of monomineralic grains, the fundamental constituent of geological samples [2,3]. With this instrument, significant progress has been achieved in the area of trace element geochemistry, particularly in igneous mineralogy leading to new methods of exploration.

The development of AMS was carried out mainly in recognition of its importance in geochronology, based on cosmogenic light radioisotopes. The research interest of the Division lies mainly in the applications of ^{10}Be and ^{36}Cl dating to problems relevant to exploration and mining. The scope of published work on applications of ^{10}Be [4], ranging from soil transport and erosion studies, rock exposure ages on to petroleum dating offers exciting prospects in research of ore and petroleum genesis as aids in exploration. Similarly, the information from ^{36}Cl as a tracer and chronometer of groundwater can be an important supplement in hydrogeochemical methods of exploration, and water management in arid areas. In addition to the direct requirements in the minerals industry, HIAF is accessible by other areas of research, and thus the AMS facility will also be available for ^{14}C dating.

Of more direct interest to minerals research is the AMS capability to detect very low levels (ppb) of trace elements. So far the method has been applied using a submillimeter sputtering beam, which is not adequate for most measurements requiring monomineralic in situ microanalysis [5]. A microprobing sputter source must be developed for successful applications of AMS as a trace analyzer.

2. The AMS system

The HIAF-AMS project will proceed in two stages, with the first resulting in standard AMS capability, viz. ^{10}Be , ^{14}C dating on "bulk" samples. ^{36}Cl detection will also be attempted. The second stage involves the development of the microprobing Cs sputter source. The AMS system incorporates the existing beam transport system at HIAF, with the addition of a beamline for the detection system, and a separate injector.

A schematic of the HIAF beam transport system, including the AMS system, is shown in fig. 1. The AMS injector system is based on a double focusing, 90° analyzing magnet with a radius of 30 cm and beam product (ME/q^2 in amu MeV/e² units) of 7, with a maximum, aberration-limited momentum resolution of 6500 for an object diameter of 0.25 mm. For normal operation using typical ion sources, a more moderate resolution is expected for good transmission efficiency through the accelerator. The magnet box is electrically insulated from the rest of the beamline to permit energy modulation of the incident beam ("bouncing") to maintain the same magnetic rigidity. A 90° electrostatic spherical analyzer with 75 cm radius preceding the magnet will be added in the future, to improve the rejection ratio of adjacent isotopes.

The beam from a General Ionex model 834 Hiconex sputter source is focused by an einzel lens to form a waist at the magnet's object slits. The beam is further transported to the original low-energy cup through the "old", demagnetized injector, by means of another einzel lens. Distances are chosen to match the emittance of the AMS injector system to the acceptance of the original system. The "cone" of the Hiconex source, which holds the sample to be sputtered, is modified to permit focusing of the Cs beam onto the downstream side, and into a smaller area. The sample is loaded into a "well" in the cone (1 mm diameter and 1 mm deep). This modification reduces the amount of sample required and improves the source emittance.

An AMS facility for minerals exploration research

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Section VIII. Geological and mineralogical applications

The proton microprobe: a revolution in mineral analysis

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Application of the proton microprobe as a quantitative tool for trace-element microanalysis in the geosciences can be considered to have crossed the threshold of acceptability in a number of areas, particularly in igneous and metamorphic mineralogy and petrology. In the minerals industry, applications in base metal ore mineralogy provide new data useful for both processing and genetic studies. Applications in diamond and gold exploration are developing into new methods, with potential widespread acceptance. The paper will review a few case histories, and discuss the limitations of the current state-of-art and conditions conducive to widespread acceptance by geoscientists and by the minerals industry.

1. Introduction

The anticipated benefits of the proton microprobe applications in the geoscience have been realized in an ever increasing number of areas, marked by the progression from experimentation to routine application of the technique. Better access to accelerator facilities by geoscientists, close links between physicists and geoscientists, and dedicated facilities are requisites of this progress. Such conditions apply in a number of laboratories, notably at Heidelberg, Witwatersrand and Los Alamos [1–3]. HIAF is an example of a dedicated facility, established to enable sustained development of the applications in the geosciences, and promote the introduction of accelerator-based analytical methods into the mineral industry [4]. This includes not only the proton microprobe [5], but other ion beam analysis (IBA) methods and accelerator mass spectrometry (AMS) as well. In Australia this is warranted by the important role of the mineral industry in the national economy.

The statistical nature of geological samples and data requires analysis of large numbers of samples, and the interpretation often depends critically on the accuracy of the data. Speed of analysis governs the viability of the method, particularly in the industrial context, affecting among others the cost factor. With appropriate design of both hardware [5] and software [6] these requirements can be fulfilled successfully.

While experimentation continues, significant progress has been achieved over the past few years. In particular, quantitative analytical micro-PIXE has found

an appropriate niche in igneous mineralogy and petrology, marked by contribution to advances in the mainstream areas. In sulfide mineralogy, trace-element data have contributed to the understanding of ore genesis and found direct application in exploration and processing of base metal ores. The present paper reviews the potential and constraints of analytical micro-PIXE, and presents a few case histories for illustration.

2. The proton microprobe

The applications of the proton microprobe in general have developed along two virtually separate lines. In one the emphasis is on imaging and on the attainment of the best resolution, with the scanning mode as the main mode of operation [7,8]. The other concentrates on its use as a quantitative microanalytical tool [6,9], with resolution considered as a second priority. The latter has been the line adopted at HIAF for geoscientific applications. Progress in this has been reviewed in a number of recent papers [11–13], and is the subject of the present paper.

One emerging conclusion is that quantitative micro-PIXE in the geosciences has graduated from being an experimental tool, into a vital tool for the progress in a number of specific areas. The successes achieved thus far have been based mainly on adaptation of electron microbeam methodology, i.e. nondestructive in-situ trace-element analysis by induced X-ray spectrometry. The better sensitivity (as low as < 1 ppm) afforded by the lower bremsstrahlung revealed new information hitherto inaccessible or tedious to obtain. However, one has to be continually aware of alternative [14], and

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APPLICATION OF THE PROTON MICROPROBE TO DIAMOND EXPLORATION AND GENESIS

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Heavy Ion Analytical Facility, B-15, 2233 Division of Exploration Geoscience, North Ryde, NSW 2113, Australia

The HIAF proton microprobe is being used to analyze trace elements in mantle-derived minerals, including garnets, ilmenites, and chromites. The goals are to understand mantle processes and to improve the use of indicator minerals in diamond exploration programs. Interpretation of the data provides new information on magma compositions and fractionation mechanisms, metasomatic processes, time scales of heating and melt infiltration, and the environment of diamond formation. Trace-element data on indicator minerals improve discrimination between barren and diamondiferous source rocks, and help to recognize the presence of multiple source rocks within one drainage. They will also ultimately help to improve the models that guide exploration.

1. Introduction

Diamonds are formed at depths of more than 150 km in the Earth's mantle, and carried to the surface during volcanic eruptions of special rock types, such as kimberlite or lamproite. The diamond content of such rocks is typically a few ppm. Exploration for diamonds therefore is heavily based on the recognition of more abundant mantle-derived "indicator minerals" (Cr-pyrope garnet, Mg-rich ilmenite, chromite) in samples of soil and stream sediments.

Electron microprobe analyses of indicator minerals give the major-element composition of individual grains. These data are used during exploration and during evaluation of prospects, to assess the probability that particular samples are derived from diamondiferous rocks. However, this method is commonly criticized because minerals of similar major-element composition also may be derived from a range of barren rocks.

Since 1987, HIAF has carried out a program of proton microprobe analysis of trace elements in indicator minerals, aimed at adding a new dimension to discrimination in this exploration field. The material being analyzed consists of heavy-mineral concentrates from diamondiferous and barren rocks. It provides empirical discrimination between barren and diamondiferous rocks by measuring trace elements in the minerals in fragments of xenoliths and megacrysts, often in the same kimberlites, and the mineral inclusions in diamonds. These studies provide insight into the metamorphic processes in the mantle, and are valuable for the formation of models that guide exploration. This report will emphasize the results of studies of xenoliths and inclusions in diamonds.

2. Methods

The analytical methods used in this work have been reported elsewhere [1,2] and a detailed treatment of the HIAF hardware and software is given by Ryan et al. [3-5]. Mineralogical applications of the proton microprobe, especially those reported here, require large numbers of accurate, high-precision analyses. The HIAF hardware [6] has been specifically designed to allow high sample throughput, with high beam currents for low detection limits, flexible sample handling and minimum cycling times for sample changes. The software development has concentrated on ease of use and reliability of data treatment, with special attention given to the development of stable background algorithms for the reproducible treatment of low-statistics peaks [3,5]. For most of the PIXE microanalysis reported here, a 8 nA 3 MeV proton beam was used, with a beam spot size of 20 μm . A 200 μm Al X-ray absorber is usually selected to attenuate major-element lines. The typical integrated charge was 3 μC , corresponding to an acquisition time of 6 min per grain.

3. Results

3.1. Garnets

The grains of Cr-pyrope garnet $((\text{Mg}, \text{Fe})_3(\text{Al}, \text{Cr})_2\text{Si}_3\text{O}_{12})$ found in heavy-mineral concentrates from volcanic rocks are derived largely from the disaggregation of xenoliths of mantle wall rocks such as garnet peridotite. Griffin et al. [7] showed that the distribution of Ni between Cr-pyrope garnet and olivine in such xenoliths is strongly dependent on T , as mea-



**APPLICATION OF THE PROTON MICROPROBE IN MINERAL EXPLORATION
AND PROCESSING**

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The in situ high-sensitivity multielement detection capability of PIXE, combined with μm spatial resolution opens up new possibilities in mineral-related research. Trace element data obtained using the proton microprobe provide new tools in exploration for diamond and precious metals, ore genesis studies as well as in the processing of precious-metal-bearing ores. Introduction of this new methodology to the minerals industry however is controlled by economic factors which must be taken into consideration.

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IN PHYSICS RESEARCH B**

AN ACCELERATOR FACILITY WITHIN A MINERAL RESEARCH ESTABLISHMENT

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The importance of the minerals industry in Australia is evident from its share of about 40% of the country's export earnings. Its economic success is due in no small measure to the industry's ability to keep abreast with technological innovations and scientific developments, often through collaborations with federal Governments research laboratories such as the CSIRO. In this context, the CSIRO Division of Mineral Physics recently commissioned a Laboratory, known as HIAF - the Heavy Ion Analytical Facility - based on a General Ionex 3 MV Tandetron, a tandem electrostatic accelerator. The Laboratory was designed to facilitate the development of the applications of a host of ion-beam techniques to problems in the geosciences, extending or complementing established methods. Flow-on to the minerals industry is anticipated, with varying degrees of immediacy dependent on the particular technique. The first stage operational at the commissioning provides RBS (Rutherford backscattering spectrometry), PIXE (particle induced X-ray emission) and NRA (nuclear reaction analysis) measurements, and includes the development of a beam microprobe. An ultra-sensitive accelerator mass spectrometry (AMS) system is planned for the second stage, to permit studies of chronology based on radio cosmogenic isotopes and ultra-traces in mineral samples.

1. Introduction

The Australian minerals industry expanded rapidly during the past two decades and became an important part in the country's economy. In its peak year of 1981-82, the industry generated about 40% of the export earnings [1]. One contributing factor to the success of the industry is its ability to keep abreast with technological and scientific developments in all its stages, from exploration, mining on to beneficiation process, this ability is bolstered by the Federal and State governments involvement through bodies such as Geological Survey bureaus and research laboratories such as the CSIRO Minerals Research Laboratories as it was originally known, now part of the larger Institute of Energy and Earth Resources. Collaborative efforts between the industry and government laboratories proved effective in the introduction and development of various advanced techniques.

The Division of Mineral Physics played a considerable role in a number of cases: the transient electromagnetic technique for prospecting of buried ore bodies, the use of Landsat images as aid in explorations and adaptation of nuclear techniques in mining and beneficiation. The decision by the Division to acquire an accelerator laboratory can be viewed as a continuation of this tradition. The Laboratory, known as HIAF - the Heavy Ion Analytical Facility - was conceived in the recognition of the demonstrated and potential applications of ion-beam techniques to geological and mineralogical problems, as well as in other research areas of interest to the Institute. Applications of accelerator

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Of immediate interest is the application of standard ion-beam techniques, namely the RBS (Rutherford backscattering spectrometry), NRA (Nuclear Reaction Analysis) and PIXE (particle Induced X-ray Emission).

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Crystallography	XRD (gross structure)	RBS-channeling (atomic location of impurities)
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Depth profiling	(ion-microprobe) depth resolution ~ 10 Å range < 1 µ	NRA (depth resolution ~ 10 nm range several µm)

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The advent of AMS (Accelerator Mass Spectrometry) presents yet another tool which is even more directly applicable to geological problems. Table 1 summarizes a number of typical analyses required in minerals research and the ion-beam techniques are juxtaposed as an extension or as a complement to established techniques.

This paper describes briefly the development of the laboratory. Some preliminary results are presented to illustrate the utility of accelerator-based techniques in the earth sciences, and in minerals research in particular.

2. The Laboratory

The selection for a suitable accelerator was governed by a number of criteria:

- the accelerator must enable all ion beam techniques applications, including the AMS;
- since the Division has no established infra-structure comparable to that found typically in physics departments, the accelerator must be relatively easy to operate and maintain;
- the variety of techniques requires a flexible machine, where change of ion species and variation in energies can be effected expeditiously;
- an extra criterion set by other interests in the Institute is that the accelerator should be capable of producing heavy ion beams of relatively low energies (< 500 keV), comparable to that obtainable with ion-implanters.

The first three criteria lead naturally to the specifications for a tandem electrostatic accelerator, with a minimum terminal voltage of at least 2 MV.

The General Ionex Co. won the tender for the supply of a 2.25 MV Tandatron, which was subsequently upgraded to 3 MV. The accelerator was delivered in mid 1983 and acceptance tests were carried out in September 1983 (see table 2). Although the laboratory was officially opened in October 1983, tests and development continued well into 1984. Fig. 1 shows the layout of the laboratory, which occupies the ground-floor of a new three storey building. Up to five beam lines will be installed ultimately. Fig. 2 is the photograph of the accelerator hall, showing the two beam lines operational at commissioning. All experimental apparatus pass the switching magnet were designed and built by the Division to ultra-high vacuum standards. The first beam line permits RBS, NRA and PIXE measurements. The second beam line is a dedicated microprobe. A set of electrostatic quadrupole lens with the "Russian quadruplet" configuration is used to shape the beam to microns dimensions [2]. The specimen chamber includes a Si(Li) detector and provisions for a wavelength dispersive system to be installed at a later date, and a normal viewing microscope with 400 $\times$ magnification.

Table 2

Acceptance test at General Ionex Corp. (February 1983) and in Sydney (September 1983)

Terminal voltage	
conditioning:	+ 2.6 MV (at GIC), 2.8 MV in Sydney
with beam (protons):	2.4 $\rightarrow$ 2.5 MV
ripple (DVM-GVM):	0.3–0.7 kV
Analyzed beam currents:	
1. Direct extraction Duo Plasmatron:	
protons:	> 10 μ A, $E = 5.0$ MeV
	> 10 μ A, $E = 0.4$ MeV
	($\sim 50\%$ transmission)
oxygen (O^{3+}):	12 μ A, $E = 9.0$ MeV
2. D.P. (+ve)+Li exchange canal	
Alphas (He^{2+}):	2 μ A, $E = 6.75$ MeV
3. Hiconex sputter source:	
Si (3^+):	3 μ A, $E = 6.4$ MeV (max rigidity)
Ni (3^+):	46 nA, $E = 3.0$ MeV
S (3^+):	3 μ A, $E = 6.0$ MeV
C (3^+):	15 μ A, $E = 9.0$ MeV
N 14 (3^+):	0.5 μ A, $E = 9.0$ MeV

Particular care was observed during the accelerator installation to the alignment, cleanliness of vacuum components and the pressure vessel. The laboratory floor was preloaded prior to the arrival of the accelerator with simulated weight of the system, to ensure that no change can occur after the installation. Thorough cleaning of vacuum parts, particularly the accelerator tubes, resulted in a vacuum of 6×10^{-8} Torr in the tubes. The pressure vessel was alternately evacuated to 20 μ m Hg and backfilled with dry N_2 a few times prior to charging with the SF_6 insulating gas. The moisture content of the SF_6 in the pressure vessel was found to be stable at around 90 parts-per-million (ppm) eliminating the need for a drying system. A cryogenic SF_6 gas handling system was built which minimizes contamination sources by eliminating the need for compressors. The system consists of a bank of Al gas cylinders which can be cooled by immersion in liquid nitrogen when storing the gas from the tank. The reverse cycle is simply effected by heating the cylinders to provide the latent heat of evaporation.

The accelerator voltage was calibrated by means of the $^{19}F(p, \gamma)^{16}O^*$ resonance at $E_p = 0.8721$ MeV, $^7Li(p, n)^7Be$ and $^{19}F(p, n)^{19}Ne$ neutron thresholds at $E_p = 1.8806$ and 4.2343 MeV respectively [3] on a thick LiF target. The analyzing magnet field is measured with a Rawson probe. Over the period of 8 months we found that the energy stability of accelerator is excellent, as can be observed in experiments involving resonances, such as hydrogen profiling described further below. There was no evidence of long term drift, the reproducibility of terminal voltage over the same period is better than 0.5 kV. This is remarkable considering that there is

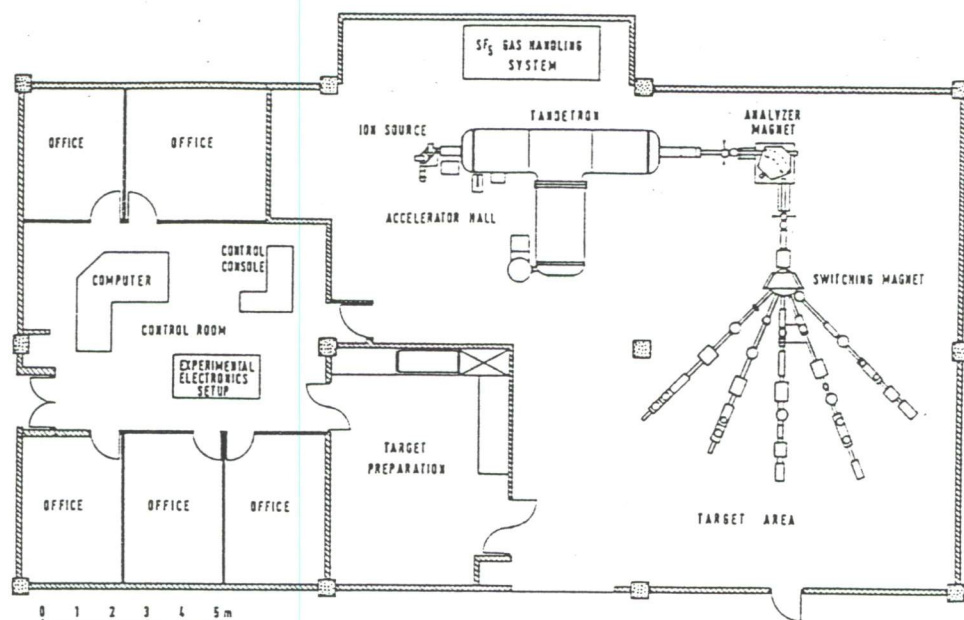


Fig. 1. Schematic lay-out of the HIAF Laboratory at the CSIRO Institute of Energy and Earth Resources, Sydney, Australia. Two out of the ultimate five beam lines are operational currently.

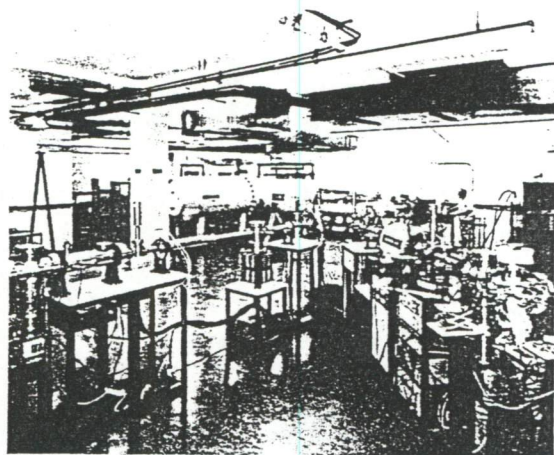


Fig. 2. A view of the accelerator hall showing the Tandatron in the background and the two beam lines in the foreground. All beam lines are constructed to UHV standard.

no analyzing slits stabilization system, such as that used on Van de Graaffs.

3. Experimental programme

3.1. PIXE

The importance of this technique is apparent from the fact that its sensitivity at a few ppm is at least two

orders of magnitude better than can be obtained with electron microprobes. Fig. 3 shows a PIXE spectrum obtained from a US Geological Survey Standard "5 ppm" glass (GSC) using 3 MeV protons. A 400 μm Al absorber was used to suppress lines from the major elements, mainly below Fe. It can be seen that 5 ppm for medium mass elements can be detected quite readily.

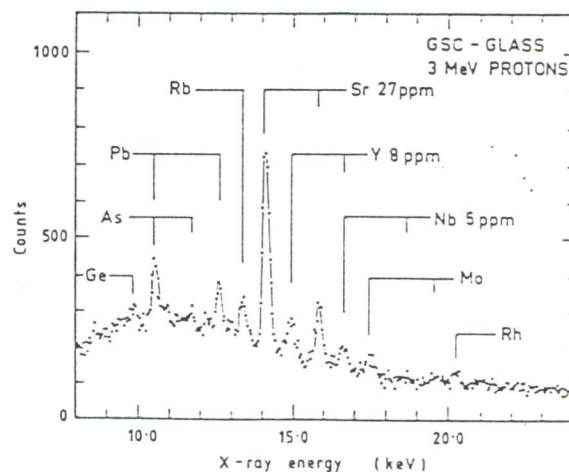


Fig. 3. PIXE spectrum obtained with 3 MeV protons of a standard glass containing a cocktail of trace elements. A 400 μm Al absorber was used to suppress major lines. It can be seen that 5 ppm level can be detected readily.

For mineralogical applications, a microbeam is necessary to enable probing of coexisting mineral phases which typically would be a few tens of microns dimension.

Electrostatic lenses offer a few advantages over magnetic ones, particularly when used with electrostatic accelerators. Excitation of the lens is proportional to $E/q = (q+1)V/q$, where E and q are the beam energy and charge state respectively, V is the terminal voltage. The excitation is thus completely independent of the mass of the beam projectile m , whereas magnetic lenses would require an excitation proportional to m/q which may not be realizable for heavy ions. Another advantage is that electrostatic lenses are amenable to miniaturization, enabling compact lenses to be built, in turn liberating more space for other uses such as the wavelength dispersive detector system planned for HIAF.

The electrostatic quadruplet lens at HIAF has been constructed with minimal adjustment, and relied instead on the best possible mechanical precision for alignment of the components. Preliminary test on-line yielded a 20 μm beam spot with a coarse object slits. An object aperture with a defined dimension will be installed shortly.

Trace element distribution plays an important role in studies of mineral and ore genesis, an in geochemical methods of exploration for concealed deposits. In the last decade some 20 major deposits and even more smaller ones ranging from porphyry and massive sulphide types to gold-silver veins and pegmatites have been discovered by geochemical techniques [3]. The methods are based mainly on areal surveys of secondary dispersion haloes and trains in media such as surface waters, soils and drainage sediments. A number of techniques are available for detection of elements at trace levels (<1000 ppm), based mainly on optical emission or absorption, but they are invariably destructive thus incapable of giving in-situ information. Erroneous information can arise due to concentration of trace elements in inclusions and imperfections in the mineral's crystalline structure.

One example of potentially major application of PIXE with a microprobe is in the study of pathfinder minerals. Fig. 4 shows the two spectra obtained from ilmenite (FeTiO_3) found commonly in igneous rocks. Again the spectra were obtained with 3 MeV protons and a 400 μm Al absorber was used to suppress the major elements. The importance of using a microprobe can be understood when one examines the photo micrograph of the mineral grain (fig. 5), showing extensive pitting and cracks where anomalous concentrations of certain trace elements may occur. Data were obtained from parts of the grain with clear surface, and the two spectra show a contrast of the content of trace elements Zr and Nb obtained from two grains from different

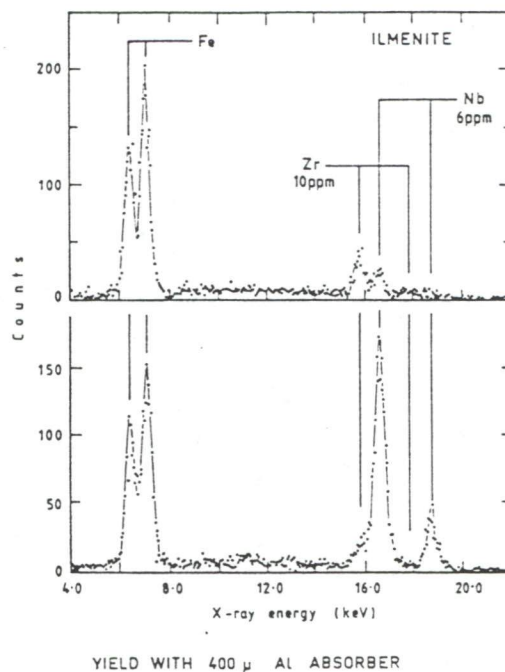


Fig. 4. PIXE spectra obtained with 3 MeV protons microbeam of 2 samples of ilmenite (FeTiO_3) from two different sources, showing the contrast of the trace elements Zr and Nb. The major lines are suppressed by the 400 μm Al absorber.

sources. The object of the study is to investigate whether there are systematic differences in characteristics of the trace element distribution in this mineral found in barren areas and in formations containing economic miner-

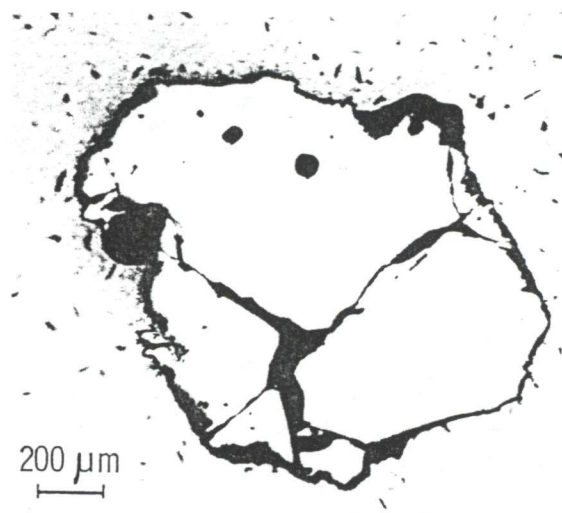


Fig. 5. A photograph of one of the grains of ilmenite mineral used to obtain the spectra in fig. 4. A microbeam is needed to avoid the pits and inclusions in the mineral which will give erroneous trace element concentrations.

als such as diamonds in kimberlites. Such a study requires extensive accumulation of data, to establish any possible trend.

The PIXE technique with energy dispersive detectors is necessarily limited to detection of elements heavier than Na, due to the absorbers needed to protect the detector from scattered beam. This limit can be pushed towards lower Z when a heavier beam is used to induce the fluorescence, requiring thinner absorber.

3.2. RBS

Detection of low Z elements, particularly H, C, N, O, F are of interest in geological and minerals research, as they are present in virtually all minerals. The RBS technique and NRA as will be discussed further below, can be used to complement PIXE for detection of light elements. A variation of the RBS technique exploiting resonant scattering provides an alternative method of profiling. For example, a strong resonance at alpha bombarding energy of 3.0359 MeV can be exploited to detect and depth profile oxygen [5]. This is illustrated in fig. 6 showing spectra obtained from a mineral pyrrhotite – a nonstoichiometric compound of general formula Fe_{1-x}S , where X can vary from 0 to 0.21. Oxygen plays an important role in determining the stability of the various compounds, particularly monoclinic pyrrhotite ($X = 0.125$). The oxygen can be detected readily as can be seen in the figure. Normal RBS does give sufficient sensitivity, particularly on thick samples. The resonance enhances the oxygen detection, illustrated dramatically in part b of the figure obtained from quartz, where oxygen is present in large quantity (67% atomic). The oxygen must be determined in-situ with a microbeam to avoid micro-inclusions of oxides and silicates.

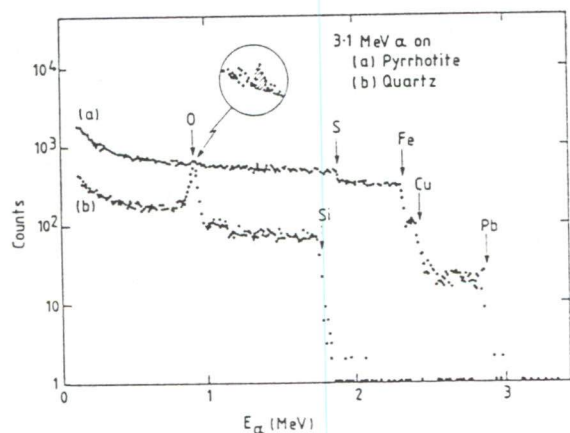


Fig. 6. RBS spectra from (a) pyrrhotite and (b) quartz showing the resonant oxygen peak. The bombarding energy is higher than the resonance $^{16}\text{O}(\alpha, \alpha')$ at $E_R = 3.0359$ MeV, thus the peaks observed originate from sub-surface oxygen.

The use of RBS in crystallographic study through the channeling phenomenon is well established, with most applications in the semiconductor study. Extension of these applications in mineral crystallography can be anticipated to yield new information.

3.3. NRA

The role of NRA in hydrogen profiling is well documented [6]. One application of interest in geotectonic study is in the measurement of the rate of diffusion of water in quartz, a major constituent of most rocks, under high pressure and temperature such as that obtaining in the earth's crust. The phenomenon "hydrolytic weakening" in quartz [7], the increase of plasticity with increasing water content, has so far been studied mainly by means of infrared spectroscopy for the detection of the hydroxyl, which does not yield depth distribution information. A systematic study to elucidate the problem has begun at HIAF. Fig. 7 shows an example of hydrogen profile obtained from a synthetic quartz hydrated under high pressure and temperature.

The data were obtained with the $\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}^*$ reaction at resonant energy 6.417 MeV. Although this resonance is not as strong as the more commonly used one at 16.44 MeV, it gives a better depth resolution and longer range of applicability. The ^{15}N reaction at 6.385 MeV gives even better resolution, but the beam is not as easily produced in a tandem accelerator as ^{19}F .

Future development to increase the H detection sensitivity includes a low background system similar to that developed at Heidelberg [8] or the forward recoil spectrometry method [9].

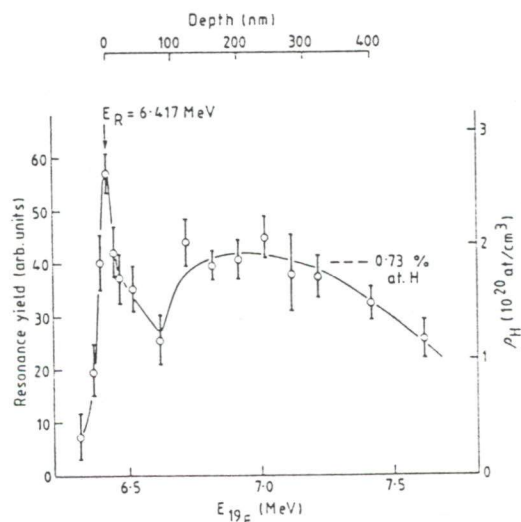


Fig. 7. Hydrogen profile of a synthetic quartz hydrated at high temperature and pressure. The surface peak represents moisture adsorbed on the surface. The data can be unravelled to deduce the diffusion rate of water.

Table 3
Application of ^{10}Be and ^{36}Cl dating by AMS

^{10}Be ($T_{1/2} = 1.5 \times 10^6 \text{ y}$)
climatology from study of ice cores
cosmic ray variation from study of sediments
global production rate from rainfall study
ocean floor subduction from study of volcanic rocks
age of marine phosphorities
mineral nodules study
dating of petroleum
soil study for erosion, weathering
surface exposure age of rocks
meteoritic impact ejects
^{36}Cl ($T_{1/2} = 3 \times 10^5 \text{ y}$)
hydrology: groundwater in Arizona
Great Artesian Basin
Milk River Aquifer
radioactive waste repository evaluation

3.4. AMS

The relevance of AMS to the geosciences became more apparent with the increasing number of applications [10]. Its significance in the ^{14}C dating is now firmly established. More important to the geosciences is the application of ^{10}Be and ^{36}Cl dating. A summary, by no means complete, of applications to date is shown in table 3.

In addition, with a microprobing source the AMS will extend the range of the best of current conventional ion-microprobe, not only for isotopic analysis, but also for in-situ ultra-trace detection (parts-per-billion ranges).

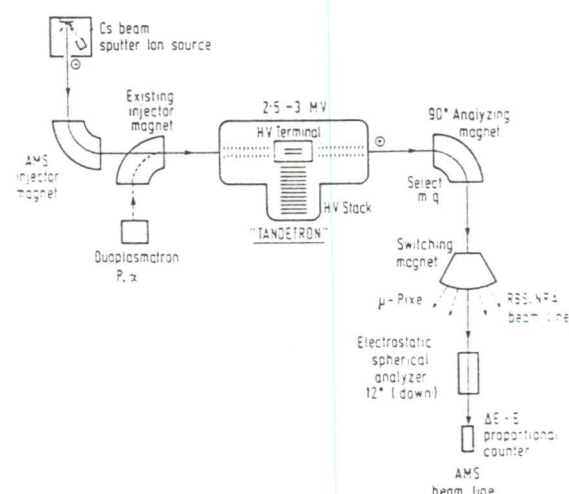


Fig. 8. Schematic diagram of the AMS system planned for the HIAF laboratory. A separate injector will be added, and the detector system including a spherical electrostatic analyzer will be installed as one of the beam lines.

The system planned for HIAF is shown in fig. 8. A double focusing magnet with a moderately high resolution ($M/\Delta M > 800$) will be added as a separate injector. The E/q analysis follows the m/q analysis, as practised in a number of laboratories. This has the disadvantages in the need to alter the analysing magnet setting for injection of the various isotopes. With the eventual computerized control of the beam transport components, this does not present a severe drawback.

5. Summary

A 3 MV Tandatron Accelerator was installed at the Heavy Ion Analytical Facility (HIAF) of the CSIRO Division of Mineral Physics at North Ryde, a suburb of Sydney, Australia. The laboratory was designed to facilitate development and applications of ion-beam techniques in the geosciences, with the anticipated flow-on to the minerals industry. Initially, established techniques of RBS, NRA and PIXE, including a microprobe, will be utilized, and these can be considered as an extension or complementary to conventional analytical tools at the geoscientist's disposal. In addition, an accelerator mass spectrometry system, with obvious important application in the geochronology and trace element studies, will be developed.

One key ingredient to ensure the success of such facility is the ease of operation and maintenance from the user's and support staff points of view. The choice of a Tandatron appears to have fulfilled these aims, despite minor problems encountered at the beginning.

The author wishes to thank the staff at the Division of Mineral Physics, and the general site staff at the Institute for their prodigious effort and skill in the installation and development of the laboratory. The Division of Mineralogy contributed in the development of the microprobe. General Ionex cooperativeness during the whole project is gratefully acknowledged. Special thanks are due to C. Ryan, G. Suter, J. Pearson and C. Dawson on site and to K. Purser, A. Petersen, R. Schneider, D. Mills and T. Smick at General Ionex.

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**APPLICATION OF THE PROTON MICROPROBE IN MINERAL EXPLORATION
AND PROCESSING**

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The in situ high-sensitivity multielement detection capability of PIXE, combined with μm spatial resolution opens up new possibilities in mineral-related research. Trace element data obtained using the proton microprobe provide new tools in exploration for diamond and precious metals, ore genesis studies as well as in the processing of precious-metal-bearing ores. Introduction of this new methodology to the minerals industry however is controlled by economic factors which must be taken into consideration.

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1. Introduction

Accelerator-based analytical methods' applications in the geosciences expanded rapidly within the past decade, as more laboratories developed stronger links with geoscience establishments. Such links became the foundation of the establishment of the CSIRO HIAF laboratory, warranted by the importance of the minerals industry in the Australian economy [1].

Among the methods, PIXE is the most readily adapted one, being closely related to the established electron microprobe (EMP). With detection limits of approximately up to a hundredfold better than those of the EMP, it offers new possibilities in trace-element geochemistry, with implications in both geology and exploration research. For example, it can provide partition coefficients of trace elements among coexisting mineral phases or the distribution of certain elements (zoning) in a single grain. These are key data for understanding the physicochemical control of geological processes, a subset of which is the ore genesis. In exploration, the signature of elements at trace levels in pathfinder minerals can yield discriminants to distinguish barren prospects. Distribution of trace elements around a prospect of concealed ore deposit can improve targeting.

The use of microbeams in the analysis is often crucial: in natural and laboratory-synthesized samples coexisting mineral phases are usually minute, typically a few μm in dimensions; zoning occurs on μm scale; in processing ores comminution to μm size is typical. However, while it may be desirable to use the smallest beam possible, usually at the expense of beam intensity, this must be balanced against the fact that the range of proton beams used in PIXE (2–4 MeV) is of the order of 50 μm in most minerals, although the effective depth of X-ray production is less (10–20 μm). Therefore, it

may not be advisable to analyze grains with sizes less than a few tens of μm , to avoid complications due to underlying or overlapping phases.

Extending the applications to the minerals industry adds another dimension, namely the cost factor, to the general problem of introducing a novel methodology. In contrast to academic applications where usually a limited number of analyses on a limited number of samples are sufficient, industrial applications deal with much larger numbers of samples. Hence the cost of analyses must be reduced in order to make the method viable in view of competing with conventional methods. This can be offset by the uniqueness of the information or by superior quality of the data obtained. Economic considerations are of paramount importance in an industry controlled by commodity market fluctuations which in turn govern the areas for development of applications. In the following, examples are presented which reflect this constraint.

2. The instrument

The design of a microprobe system is invariably dictated by the intended use of the facility. In a recent review, Cabri [2] listed attributes of an ideal system from a mineralogical perspective.

The CSIRO HIAF microprobe system is part of an analytical laboratory, based on a General Ionex 3 MeV Tandatron. The laboratory was designed to enable applications of the complete suite of ion-beam analytical methods (RBS, NRA) including accelerator mass spectrometry (AMS). The microprobe system is based on an electrostatic "Russian" quadruplet lens [3]. There is considerable overlap between Cabri's list and the following features which were implemented at HIAF in view of the perceived requirements for geoscientific and in-

dustrial applications:

- Practical beam currents (1–20 nA) at 5–20 μm resolution for viable analysis time for traces at the ppm level;
- ability to view the specimen at normal angle, to enable analysis of thick samples of opaque minerals, with $150\times$ magnification; this also facilitates tuning of the microbeam visually on an optically fluorescing target;
- ability to move specimens in view with microstages;
- a set of filters or combination of filters for the Si(Li) detectors readily selectable, to permit optimization of detection sensitivities of desired elements;
- rapid sample change through a vacuum lock;
- detection of radiations other than X-rays, namely backscattered particles and gamma rays;
- on-line data analysis, and rapid turnaround;
- ease of operation and maintenance;
- standardless quantitative analysis.

It is important to recognize that PIXE should not be used in isolation, but rather to complement or to be supplemented by other more conventional tools, such as EMP or optical microscopy, in view of a number of problems:

- The use of absorbers in order to protect the Si(Li) detector from scattered beam or to optimize detection sensitivity of a certain range of elements usually prevents detection of major light elements in the matrix which are required in the quantification of the data. While nominal compositions can be used if the sample is known generically, more often there are significant variations from the nominal values, which affects the results of the analysis.

- Normalization of the observed major element is also required to bypass the problem of accurate beam charge measurements. Charge buildup on targets, despite the presence of a conducting layer on the specimen surface, affects beamcharge integration unpredictably.

- It is sometimes desirable to analyze “thin” ($< 20\text{--}30\ \mu\text{m}$) sections of the specimens, either for convenience or to eliminate the possibility of unobserved overlapping grains, particularly in cases of opaque minerals. While the resultant analysis is only mildly dependent on the exact thickness, absolute quantification can only be obtained by normalization to a known concentration.

Optical microscopy is a necessary first step for mineralogical examination of ore or geological samples, if only to select or identify particular grains for detailed analysis. This is particularly important when one deals with an assemblage of clear minerals, e.g. silicates, unless sophisticated optical microscopy features such as polarisers are available on the PIXE system.

An important cornerstone in establishing PIXE as a routine analytical tool is a demonstration of the reliability of the method. At present there is considerable uncertainty in the reliability of trace element standards

themselves, particularly in microanalysis, and the methods of determination used originally to establish the published values. This could arise from possible inhomogeneity of standard material itself, or in the preparation of the specimen. Such problems apply for natural (e.g. SARM-7, BCR, AGV) and synthetic standards (e.g. USGS GSC). The reliability of the computer analysis of typical X-ray spectra for treatments of the general background and of weak peaks in the presence of interfering strong lines or relatively high background becomes of fundamental importance. A suite of computer programs have been developed which addressed these problems, and these are described in detail elsewhere [4–6].

3. Applications

3.1. Diamond exploration

An established method for diamond exploration is based on characterization of indicator heavy-minerals collected by stream and soil sampling. These indicator minerals are associated with igneous, mafic or ultramafic rocks, such as kimberlites and lamproites, which are the main sources of diamonds. The same minerals are often found as inclusions in the diamonds themselves, and the proton microprobe has been used to study their characteristics which provide information on the conditions of the diamond growth [4].

In exploration, garnets and ilmenites are commonly used, and chromites are particularly important being resistant to deep weathering. Previous schemes to differentiate diamondiferous occurrences based on major and minor element composition derived from electron probe analysis, have met with some success, particularly in the case of garnets as used for South African kimberlites. However, the applicability of the method is not universal, as evidenced by the failure of the garnet classification scheme in the Australian situation. Discriminants based on major elements often fail to identify multiple sources within a single-mineral anomaly. Chromites present a special problem, being present in a wide range of igneous rocks, including komatiites, ophiolites, gabbros and basalts which are not usually diamondiferous. Trace element data, particularly those of incompatible elements, can be a sensitive method to supplement the classification scheme, reflecting pressure- and temperature-controlled fractional crystallization effects during the evolution of the magma.

Samples of these indicators minerals collected in stream and soil sampling are usually minute, typically 0.2–1 mm in the extreme dimensions, but those in the original host rocks could be quite large (megacrysts). For the more typical small samples, preparations for analysis involve mounting them on glass slides or setting them in araldite followed by polishing. A repre-

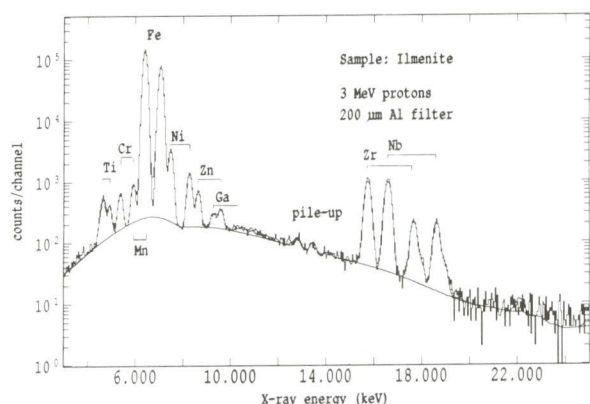


Fig. 1. A representative spectrum of ilmenite obtained with a microbeam of 3 MeV protons, including the computer fit to the data. The computed background, which includes the pileup peak contribution, is also shown. Trace elements observed are Cr, Mn, Ni, Zn, Ga, Zr and Nb at 1314, 2954, 1635, 115, 15, 286 and 339 ppm, respectively. The spectrum was obtained using a 200 μm thick Al absorber and for 0.9 μC beam charge.

representative spectrum from ilmenite is shown in fig. 1, obtained with a microbeam of 3 MeV protons. A 200 μm Al filter was used to enhance the detection of trace elements heavier than Fe. The major (Fe, Ti) and light minor elements (Mg) were obtained with an EMP, and where there are overlaps (e.g. Ti, Cr and Mn) the agreement is excellent. Fig. 2 shows the relation between trace Nb and another trace Ni and against a minor element Mg, for ilmenite from several South African kimberlites, and the limits of those obtained from basalts. The kimberlite data are separated from the basalts, and they indicate good clustering and trends in

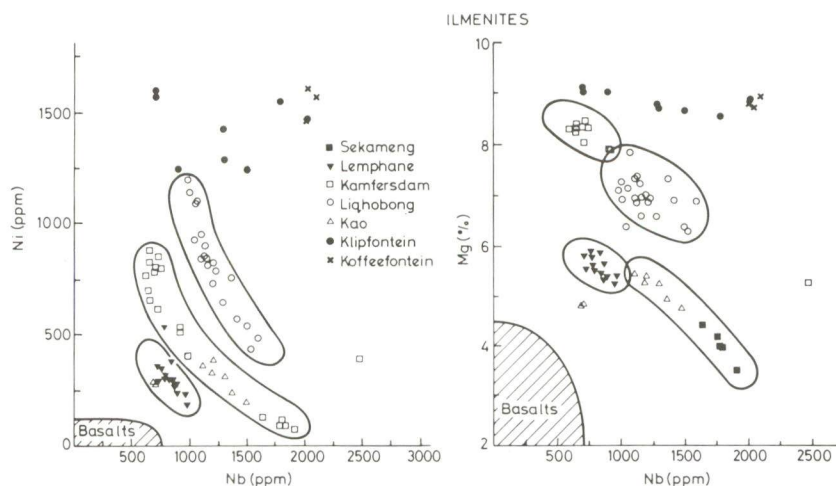


Fig. 2. Correlations between trace Nb and another trace Ni, and against a minor element Mg for several sets of samples of ilmenite from South African kimberlites. Limits of values obtained from basalts are also shown. Groupings of data from the same source shown by the hand-drawn envelopes reflect the fractional crystallization and different sources of magma, and can be used to classify unknown samples.

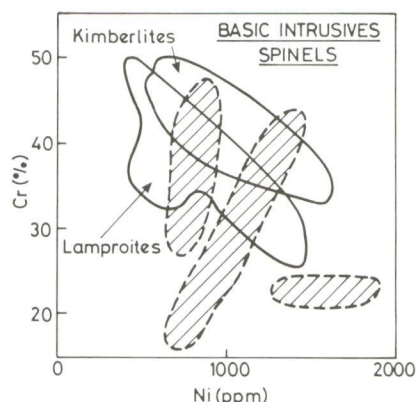


Fig. 3. Correlations between the trace element Ni in chromian spinels (chromites) against the Cr content from kimberlites, lamproites and from gabbroic intrusions show as shaded areas. The trends observed from the gabbroic intrusions are the result of competing olivine precipitation, which depletes the melt of Cr and Ni. Such information can be used in exploration programs to sort out usually nondiamondiferous gabbroic sources of chromites.

the cluster. The increase of Mg and Ni with decreasing Nb is a signature of coprecipitation of the ilmenite with olivine and garnet, and the clustering probably reflects individual small batches of crystallized magma sampled by each kimberlite. Such data demonstrate the utility of certain trace element data to identify multiple sources.

Fig. 3 shows only the envelopes of similar groups observed for chromites from kimberlites and lamproites, and from a number of gabbroic intrusive complexes shown as shaded areas. The distinct trends observed from the gabbroic sources is the result of competing

crystallization of olivine during the chromite precipitation, depletion the melt in Cr and Ni. Systematic studies such as this will eventually establish a more definitive criteria for identification of the source rocks for the indicator minerals.

3.2. Platinum

Exploration for primary sources of platinum presents a challenging problem, mainly due to the still rather poor body of knowledge on the genesis of different types of PGE deposit. While there is a possibility that for certain deposits, trace elements other than the PGE can be used in exploration, the elements themselves are often the best pathfinders. In order to develop the method it is desirable to devise a technique that enables detection of these elements at crustal abundance levels (parts per billion). Detection of the PGE at these levels has been carried out predominantly by neutron activation analysis (NAA), either directly or following a preconcentration step [7].

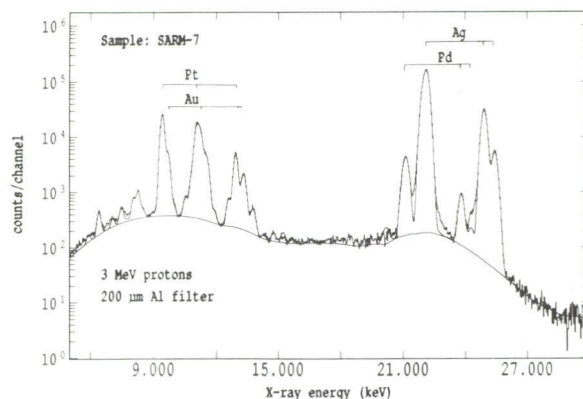


Fig. 4. A spectrum obtained from a silver prill prepared from the SARM-7 standard reference material for platinum. The fire-assay preconcentrates the precious metals (PGE and Au) by a factor of a few thousand. With a PIXE detection limit on few-ppm level in the analysis of the prill, sensitivities on few-ppb level can be obtained for the original material. The method is limited to Pt, Pd and Au. The remainder of the PGEs are either partially (Ru, Rh) or completely (Os, Ir) volatilized during the cupellation process.

Table 1
Comparison of results of prill analysis with other methods

Sample		N ^{a)}	[ppm weight]		
			Au	Pt	Pd
Ore sample C1	this measurement ^{b)}	3	8.5 (2.7)	0.49 (0.15)	1.60 (0.33)
	all measurements ^{c)}	23	7.43 (1.97)	0.45 (0.22)	1.18 (0.52)
	min ^{d)}		4.15	0.23	0.60
	max ^{d)}		11.73	0.60	3.20
Ore sample C2	this measurement	3	69.18 (8.5)	7.81 (1.39)	16.09 (1.17)
	all measurements	53	70.89 (3.76)	6.25 (1.15)	15.50 (1.29)
	min		59.47	3.29	13.13
	max		77.70	8.92	17.50
MDL			0.006	0.006	0.013
<i>Geomin standards</i>					
SS7-97/98	this measurement	2	5.64 (0.14)	1.49 (0.41)	4.96 (0.27)
	all measurements	14	6.46 (0.58)	1.77 (0.29)	5.04 (0.26)
	min		5.40	1.09	4.97
	max		7.07	2.12	5.40
SS6-701	this measurements	1	1.354 (0.012)	—	—
	all measurements	2	1.427 (0.073)		
	calculated ^{e)}		1.470		
SS6-955	this measurement	1	1.981 (0.023)	—	—
	all measurements	7	2.029 (0.025)		
	calculated ^{e)}		2.000		
<i>SARM-7 standard</i>					
Certified value			0.310 (0.015)	3.74 (0.045)	1.53 (0.03)
This measurement: Ag prill			0.532 (0.006)	3.13 (0.03)	1.727 (0.022)

^{a)} Total number of analysis.

^{b)} Mean values of results (s.d.) of the present measurements.

^{c)} Mean values of results (s.d.) of this and other measurements.

^{d)} Minimum and maximum of values for all measurements.

^{e)} Calculated value, supplied by GEOMIN.

At HIAF a method has been developed combining preconcentration by fire-assay with the PIXE method, which can achieve a detection sensitivity of 5 ppb. In the most commonly used fire-assay [8], the precious metals are extracted by fusing 20–50 g of the finely crushed ore ($\sim 75 \mu\text{m}$ particle size) with litharge (PbO) and appropriate fluxes, at around 1000°C . The noble metal collects in the resulting Pb button, which is subsequently removed by cupellation, leaving the noble metal residue, the prill. For low-grade material Ag is normally added as the concentrator, resulting in the Ag prill. During cupellation only Pt, Pd and Au remains; the other PGEs are either partially (Rh, Ru) or completely (Os, Ir) volatilized.

The Ag prills ensuing from the cupellation are analyzed by micro-PIXE, following a simple preparation involving flattening them in a holder, e.g. an Al disc or plate with suitably sized holes. The use of microbeams minimizes effects of the nonflatness of the surface. This typical prill weight in the 10–20 mg range and preconcentration factors ranging from 1000 to 10000 can be obtained. The thickness of the flattened prill is more than sufficient to stop the proton beam.

The method was tested on a number of ore samples and standards material: the SARM-7 standard [9] for PGE analysis, and another two standards obtained locally (Geomin Pty. Ltd). Fig. 4 shows the spectrum obtained from the Ag prill from the SARM-7 standard, including the computer fit to the data. In deriving the final concentrations of the elements in the prill, an iterative procedure was followed to ensure a self-consistent result for the matrix. This is particularly important for analysis of ore grade material. The homogeneity of the prill was tested by several spot analyses on the same prill.

Table 1 shows the results for the ore samples, and the GEOMIN standards, including those from other analyses carried out by conventional methods (NAA, optical emission and absorption spectroscopy), are also shown. Most of the present results agree well with the other measurements. However, the results for the SARM-7 standard show significant discrepancies with the certified values [9]. This may be attributable to possible sample inhomogeneity and variation in the fire-assay collection efficiency. The sample inhomogeneity is plausible, considering that the platinum group minerals are considerably heavier than the silicate matrix, and some settling effect can occur. In the fire assay, the effect of the flow of air in the furnace during fusion was known to produce variation in the collection efficiency [10]. However, the good agreement between the results for the other samples and other measurements imply that this is not likely in the present case. One other point to be considered also is that, although the certified values of the SARM-7 were arrived at through a round-robin analysis [9], the narrow range of

values adopted does not reflect the much larger spread in the individual results.

The results of this test indicate that micro-PIXE analysis of the prills can provide a quick and reliable method for PGE and Au determination, and with a resultant minimum detection limit at the 5 ppb level, the method can be readily applied to exploration.

3.3 Gold processing

In the beneficiation of gold ores, certain classes of ore do not yield the total gold content as determined by bulk assay. Part of the gold not liberated by the normal cyanidization is known as refractory gold. There are a number of causes of refractoriness, e.g. the presence of Cu minerals which consumes the leaching solution, and occlusion of the gold in other minerals resistant to the leaching solution. A more fundamental problem is the occurrence of gold as solid solution in other phases, such as arsenopyrite or arsenous pyrite. Roasting the ore to remobilize the Au is necessary to successfully liberate the gold. Pyrrhotite and pyrite also consume the cyanide, so unless they contain economic amounts of Au they should be removed from the concentrate. The Au distribution in the mill concentrate, or in the ore itself, can be determined by proton microprobe to formulate an optimum beneficiation strategy.

In a study of one deposit, optical microscopy of polished sections indicates that only $\sim 20\%$ of the gold assayed is present as free gold. The quartz- and dolomite-hosted deposit contains sulfide minerals, with pyrrhotite being the dominant phase at around 10% abundance. Minor phases in order of decreasing abundance include pyrite ($\sim 1\%$), arsenopyrite ($\sim 1\%$), chalcopyrite, sphalerite and rare galena and pentlandite. Initial mineralogical and metallurgical tests suggested a concentration of gold into the arsenopyrite relative to the pyrrhotite and pyrite. It was difficult to draw firm conclusions from such tests due to the intergrown nature of the ore. In order to sort out this problem, the proton microprobe was applied to study the distribution of the gold in pyrite, pyrrhotite and arsenopyrite phases in the sample.

Fig. 5 shows the spectra obtained from a selection of arsenopyrite grains in polished samples of the ore. Analysis of the pyrite and pyrrhotite grains show the same suite of trace elements, and As (table 2).

The results confirm arsenopyrite as the main carrier of gold. The gold content, however, varies considerably in the 12 grains selected for this study, and ranges from below detection limit (40 ppm) to 405 ppm. An average of 160 ppm was obtained from all grains. Zn can interfere with the detection of gold, due to the closeness of the energy of the Zn K_β line (9.572 keV) and the L_α line of gold (9.711 keV). In the present sample Zn only

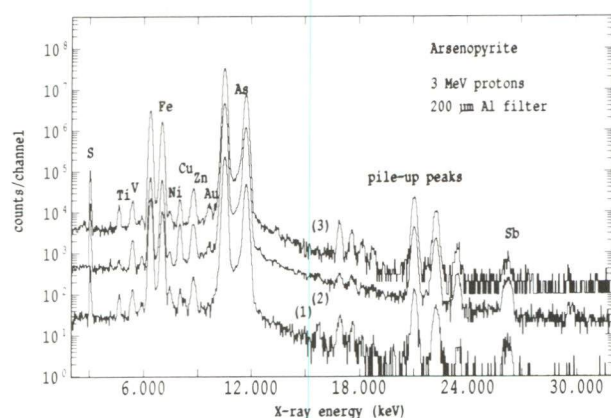


Fig. 5. A selection of X-ray spectra obtained from individual arsenopyrite grains in a refractory ore sample analyzed with a 3 MeV proton microbeam. Grains 1, 2 and 3 contain 0, 110 and 405 ppm gold, respectively. A minimum detection limit of 40 ppm is obtained, limited by the interference of the low-energy "tail" of the As K_{α} line. The Ni, Cu, Zn and S in grain 3 are 280, 380, 165 and 200 ppm, respectively. For pyrite and pyrrhotite a minimum detection limit of 5 ppm can be obtained.

occurs at levels generally below 20 ppm, eliminating the potential problem.

The pyrite analysis from the same ore sample shows a high level of arsenic (averaging ~ 1000 ppm), although the values vary from as low as 12 ppm to as high as 1%. Inclusions of arsenopyrite in the latter cannot be ruled out. The gold content from individual measurements shows levels slightly above the detection limit of 10 ppm. Analysis of the sum of runs on 16 grains gives an average value of 9 ppm with 5 ppm detection limit. For the majority of grains Au values do not correlate with As values. Sb is not detectable (≤ 8 ppm), while Se varies from 18 to 76 ppm. Analysis of the pyrrhotite

gives low levels of As (10–75 ppm) and Se (18–67 ppm). Gold values obtained are unusually at or below detection limit of 13 ppm of the individual runs. Analysis of the sum of all runs gives a 7 ppm average with a 5 ppm detection limit.

In arsenopyrite, Sb can substitute for As, and in the present case it occurs at trace levels varying from 197 to 830 ppm. Both As and Sb affect the precipitation of Au; as is believed to form a bond with Au in arsenopyrite [12] while Sb is thought to be anticorrelated with Au. The present data do not show such definite correlations. Another feature of the data is the relatively high level of Se between 116 and 400 ppm, usually associated with polymetallic-type deposits [13]. This trace element combined with sulfur data, can be used to determine the temperature in the ore paragenesis.

3.4. Silver

This precious metal is commonly obtained as a by-product of mass-metal (Zn, Cu, Pb) ore processing, with sulfide ores being the main source. Significant amounts of Ag, however, may be lost to the tailings. Silver occurs either as silver minerals (tetrahedrite, freibergite) or as solid solution in other sulfide minerals such as galena and chalcopyrite. Efficiency of recovery depends crucially on the knowledge to its distribution in the various phases. Improvement in the recovery of Ag by a few tens of ppm can translate into substantial additional revenue, considering the usually large volume of ore processed.

As solid solution, Ag occurs at levels as high as a few thousand ppm, for which electron probe analysis is quite adequate. However, at around 100 ppm it is still economic to recover, but below the detection limit of electron microprobes. Cabri et al. [14] determined the distribution of Ag and other trace elements in several massive sulfide deposits. While galena was confirmed as the most common carrier of silver, other phases such as chalcopyrite can also be important carriers [15].

In a study of a mill concentrate, bulk analysis revealed a strong correlation between silver and Pb content, shown in fig. 6. The proton microprobe was applied to study the distribution in the sample. The mill concentrate sample is set in araldite and polished for presentation to the beam. Fig. 7 shows a typical view of the sample, which consists of fragments of the sulfide and some gangue minerals recovered from the flotation circuit. Typical size of the fragments is $150 \times 50 \mu\text{m}^2$, and there is some probability that the thickness is less than $50 \mu\text{m}$. The polished surface (25 mm diameter) contains approximately 50 000 grains which were first scanned by optical microscopy at intermediate magnification. The major constituents in decreasing abundance are galena, sphalerite and gangue. Minor minerals present include chalcopyrite pyrrhotite, tetrahedrite.

Table 2

Summary of trace element concentrations [ppm] in a gold-bearing ore sample

	Arsenopyrite	Pyrite	Pyrrhotite
No. of grains analyzed	12	16	16
Au range	0– 405	0– 74	0– 36
Average, (MDL)	162 (40)	9 (5)	7 (5)
Ni	521– 800	0– 909	43–1790
Cu	241–1580	0– 85	0– 29
Zn	113– 483	0– 381	0– 24
Ga	44– 115	0– 17	0– 26
As		11–1760	10– 34
Se	116– 400	18– 76	56– 121
Sb	197– 505		
Pb		0– 29	0– 58

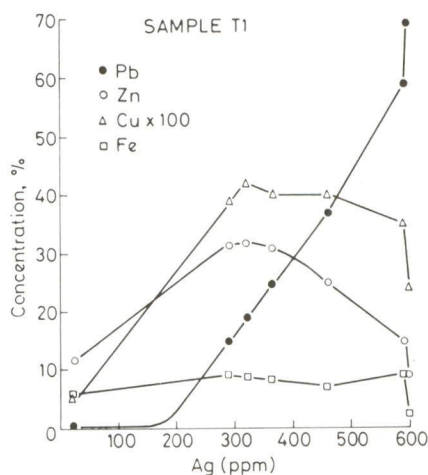


Fig. 6. Graph of the silver content against the various major elements of the base-metal sulfides in a sample of mill concentrate. A strong correlation with Pb can be seen, suggesting association of silver with galena. This is confirmed by the proton microprobe analysis of monomineralic constituents of the sample.

Representative spectra from individual monomineralic fragments are shown in fig. 8, and a summary of the results is shown in table 3. It confirms galena as a main carrier of Ag, at levels of 400–800 ppm. The average is 596 ppm, in good agreement with the Ag/Pb value of ~ 680 ppm obtained from the bulk analysis. The zero Pb intercept in fig. 6 at ~ 150 ppm Ag indicates the Ag content in other phases. The graph does not indicate linear correlation between Ag and Cu, as chalcopyrite is only a minor component in the concentrate. The Ag content of chalcopyrite is only revealed by the proton microprobe analysis, with values ranging from 210 to 940 ppm. In this sample, sphalerite does not contain

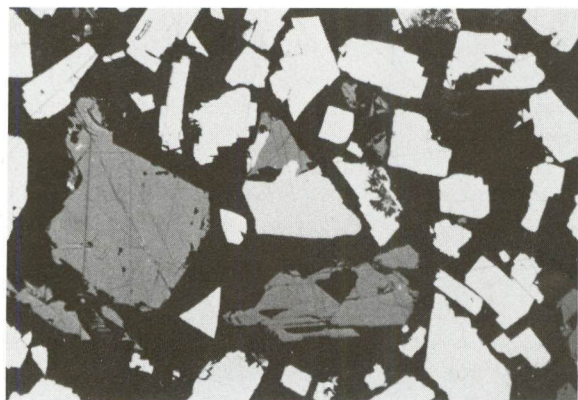


Fig. 7. A micrograph of a typical polished section made from a mill concentrate set in araldite. Fragments of separated minerals from the crushed ore are typically between 100 and 150 μm .

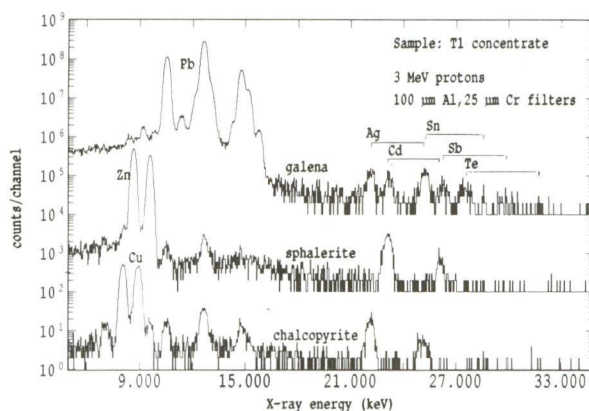


Fig. 8. Representative spectra from monomineralic fragments in the mill concentrate sample. Galena is a major component in the concentrate and can be seen to contain Ag as well as other traces. Sphalerite contains mainly Cd, and the minor component of chalcopyrite contains a significant amount of silver.

Ag; instead, Cd is the main trace element at 530 ppm to 0.17% weight. Trace Cd as well as Sb, Sn and Te are also observed in galena. Combined with a modal analysis, the trace Ag distribution can be used to evaluate the efficiency of the beneficiation process.

The distribution of the trace elements, particularly Ag, Sb and Bi (not observed, however, in the present case), can provide information on the ore genesis and metamorphism. The presence of Sb and Bi increases the solubility of Ag in galena, representing coupled substitution with valence balance of $\text{AgBi}(\text{Sb})$ for 2Pb . The ratio of $\text{Ag}/(\text{Sb} + \text{Bi})$ can be used to deduce the equilibration temperature of galena, reflecting the metamorphic or depositional temperature [16]. The detection limit for Bi in galena is relatively poor due to the interference of the Pb lines. With better resolution detectors, e.g. a wavelength-dispersive spectrometer, a more precise determination of this ratio can be made to test existing models of the genesis of massive sulfide deposits.

Table 3

Summary of trace element concentrations [ppm] in a mixed sulfide mill concentrate sample

	Galena	Sphalerite	Chalcopyrite
No. of grains analyzed	9	4	5
Ag range	324– 830	< 40– 135	213–920
Average, (MDL)	596 (40)	60 (40)	643 (50)
Cu	2600–26000	1300–8600	
Cd	90– 375	530–1700	< 50– 80
Sn		< 80	210–420
Sb	388– 2800	< 100	< 70

4. Discussion and conclusion

The examples cited above illustrate the utility of PIXE with microbeams in mineral-related problems. Trace element data in Pt-, Au-, and Ag-bearing deposits are useful both in beneficiation as well as in studies of the genesis of the deposit, which in turn can aid exploration strategy. Some of the data cannot be obtained by any other means, while some methods, e.g. the detection of Pt and Au at crustal abundances, provide an alternative and more convenient method. Invariably, however, large numbers of samples have to be analyzed and often the time factor is important in both exploration and beneficiation tests. Both require appropriate design of the hardware and software, and the cost factor can be further reduced through increased utilization of the facility and further technical improvements. Some can be readily achieved: e.g. adding another detector would immediately double the counting efficiency. Further developments are directed towards improving detection limits through better resolution or development of alternative methods. Current development at HIAF includes:

- WDS spectrometers: in PIXE interference can contribute significantly, if not dominate the MDL. WDS spectrometers offer much better energy resolution, but at the expense of detection efficiency. Development of a high-current microprobe may be required alongside this development. Areas which will benefit include detection of PGE, Au and rare-earth elements.

- Improvement in detection limit can also be achieved by selective X-ray excitation, exploiting the phenomenon of molecular orbital electron promotion induced by heavy-ion beams [17].

Widespread acceptance of the proton-microprobe-based methodology by the minerals industry is contingent upon the factors discussed above, as well as continuing accumulation of case histories. Applications of the other accelerator-based methods such as AMS, RBS and NRA remain to be developed and exploited. AMS has been shown to be capable of detecting trace element in the ppb range [18]. This method will also allow in-situ analysis of the isotopic composition of many trace elements. Application in minerals exploration is contingent upon the development of a microprobing ion source to enable analysis of individual mineral grains.

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APPLICATION OF THE PROTON MICROPROBE TO DIAMOND EXPLORATION AND GENESIS

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The HIAF proton microprobe is being used to analyze trace elements in mantle-derived minerals, including garnets, ilmenites, and chromites. The goals are to understand mantle processes and to improve the use of indicator minerals in diamond exploration programs. Interpretation of the data provides new information on magma compositions and fractionation mechanisms, metasomatic processes, time scales of heating and melt infiltration, and the environment of diamond formation. Trace-element data on indicator minerals improve discrimination between barren and diamondiferous source rocks, and help to recognize the presence of multiple source rocks within one drainage; they will also ultimately help to improve the models that guide exploration.

1. Introduction

Diamonds are formed at depths of more than 150 km in the Earth's mantle, and carried to the surface during volcanic eruptions of special rock types, such as kimberlite or lamproite. The diamond content of such rocks is typically a few ppm. Exploration for diamonds therefore is heavily based on the recognition of more abundant mantle-derived "indicator minerals" (Cr-pyrope garnet, Mg-rich ilmenite, chromite) in samples of soil and stream sediments.

Electron microprobe analyses of indicator minerals give the major-element composition of individual grains. These data are used during exploration and during evaluation of prospects, to assess the probability that particular samples are derived from diamondiferous rocks. However, this method is commonly ambiguous, because minerals of similar major-element composition also may be derived from a range of barren rock types.

Since 1987, HIAF has carried out a program of proton microprobe analysis of trace elements in indicator minerals, aimed at adding another level of discrimination to this exploration method. Much of the material being analyzed consists of heavy-mineral concentrates from diamondiferous and barren sources, to provide empirical discriminants. However, we are also analyzing the minerals in fragments of mantle rocks (xenoliths and megacrysts) carried to the surface by kimberlites, and the mineral inclusions enclosed within diamonds. These studies provide insights into rock-forming processes in the mantle, including those responsible for the formation of diamond, and help us to interpret compositional features seen in the concentrate samples. This report will emphasize results from the studies of xenoliths and inclusions in diamond.

2. Methods

The analytical methods used in this work have been reported elsewhere [1,2] and a detailed treatment of the HIAF hardware and software is given by Ryan et al. [3–5]. Mineralogical applications of the proton microprobe, especially those reported here, require large numbers of accurate, high-precision analyses. The HIAF hardware [6] has been specifically designed to allow high sample throughput, with high beam currents for low detection limits, flexible sample handling and minimum cycling times for sample changes. The software development has concentrated on ease of use and reliability of data treatment, with special attention given to the development of stable background algorithms for the reproducible treatment of low-statistics peaks [3,5]. For most of the PIXE microanalysis reported here, a 8 nA 3 MeV proton beam was used, with a beam spot size of 20 μm . A 200 μm Al X-ray absorber is usually selected to attenuate major-element lines. The typical integrated charge was 3 μC , corresponding to an acquisition time of 6 min per grain.

3. Results

3.1. Garnets

The grains of Cr-pyrope garnet ($(\text{Mg}, \text{Fe})_3\text{-(Al, Cr)}_2\text{Si}_3\text{O}_{12}$) found in heavy-mineral concentrates from volcanic rocks are derived largely from the disaggregation of xenoliths of mantle wall rocks such as garnet peridotite. Griffin et al. [7] showed that the distribution of Ni between Cr-pyrope garnet and olivine in such xenoliths is strongly dependent on T , as mea-

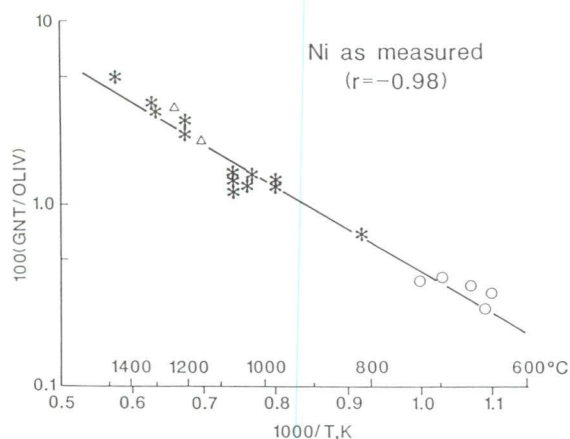


Fig. 1. Partitioning of Ni between olivine and Cr-pyroxene garnet, as a function of temperature (T ; determined by two-pyroxene or olivine-garnet thermometry). Stars, peridotite xenoliths; circles, olivine inclusions in garnet grains; triangles, olivine-garnet pairs from single diamonds [1]. From ref. [7].

sured by two-pyroxene thermometry (fig. 1). In these ultramafic rocks, the Ni content of olivine is essentially constant (2900 ± 200 ppm), while the Ni content of the garnet varies from < 20 ppm to > 120 ppm over the T range 600 – 1400°C . This makes it possible to estimate the equilibration T of a single garnet grain simply by analyzing its Ni content; the estimated uncertainty is $< 100^\circ\text{C}$.

This "Ni thermometer" has important potential as an exploration tool. The temperature-vs-depth relation (the "geotherm") is reasonably well-constrained in the stable continental areas (cratons), where most diamond exploration is concentrated. In such cratons, diamonds are only stable at depths greater than those corresponding to T of $\sim 1000^\circ\text{C}$. A kimberlite pipe or other volcanic rock will only be a potential diamond carrier if it has originated below this depth and carries a significant proportion of mantle material equilibrated at $T > 1000^\circ\text{C}$. Thus the probability that a population of garnets comes from a diamond-bearing pipe may be in part assessed by studying the distribution of Ni-temperatures in the population (fig. 2).

The Ni thermometer may also be used to identify short-lived heating and cooling episodes in the mantle, by studying the zoning of Ni within individual garnet grains. Smith et al. [8] used Ni zoning in garnets of xenoliths from the Colorado Plateau to calculate heating rates of 0.1 – 0.01°C/yr over a period of about 10000 years. These zoning profiles were frozen in when the xenolith was entrained in the magma and erupted rapidly to the surface.

Garnet grains zoned in other elements, such as Zr, Ti, Y and Ga, provide evidence on the movement of mantle melts through shear zones. Griffin et al. [2]

concluded that infiltration of magma had produced overgrowths on garnets in sheared peridotite xenoliths, and strongly modified the composition of the rocks. Modelling of zoning profiles indicated that geologically very short time scales, on the order of tens to hundreds of years prior to eruption, were involved. The results have important consequences for models of mantle

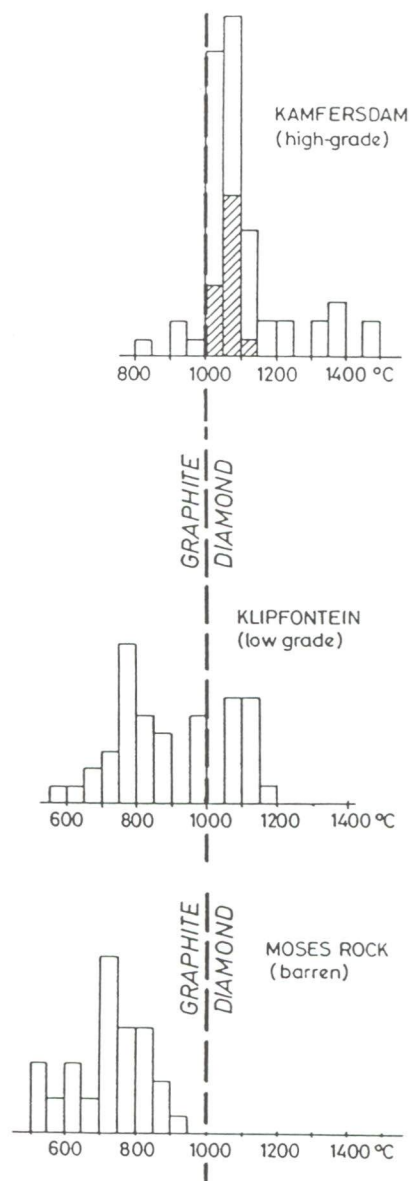


Fig. 2. Histograms of T estimates derived from single garnet grains in heavy-mineral concentrates from two African kimberlites of differing diamond content, and the barren Moses Rock diatreme (Arizona). Shaded area, subcalic garnets. The diamond/graphite line represents the intersection of a normal continental geotherm with the diamond-graphite equilibrium curve.

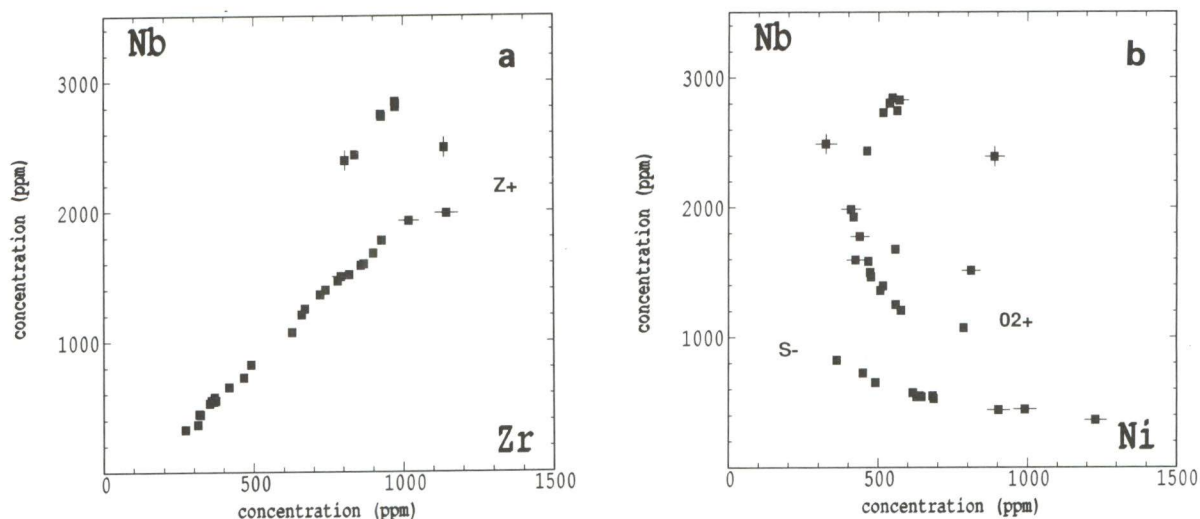


Fig. 3. Plots of Ni and Zr vs Nb in ilmenite megacrysts from the Frank Smith kimberlite pipe, South Africa. Nb increases continuously during fractionation of the magma; inflections in the curves reflect changes in the coprecipitating minerals. Z+, beginning of zircon crystallization; S-, cessation of pyroxene + garnet + olivine crystallization; O2+, beginning of second olivine crystallization. From ref. [10].

evolution; they demonstrate that the unusual compositions of these xenoliths are not, as commonly assumed, representative of long-lived mantle reservoirs.

3.2. Ilmenites

Many kimberlites carry abundant megacrysts (> 2 mm diameter) of magnesian ilmenite ((Fe, Mg)TiO₃), which is resistant to weathering and transport, and serves as an indicator mineral. The origin of the ilmenite, and its genetic relation to the kimberlite, is a matter of considerable debate. Trace-element studies of ilmenites from individual kimberlites typically show well-defined interelement trends (fig. 3). These are easily interpreted in terms of fractional crystallization of single batches of magma, in which crystallizing phases are removed from the magma (for example, by sinking) to form cumulate rocks. In a detailed study of ilmenites and coexisting silicate phases from the Monastery Mine kimberlite, Moore et al. [9] have shown that Nb behaves incompatibly, remaining concentrated in the liquid phase. Hence the Nb content of the ilmenites increases steadily throughout the fractionation sequence, while the contents of other elements, such as Ni, Zr, Ga and Ta, vary according to the nature of the coprecipitating phases (cf. fig. 3). In effect, the ilmenite serves as a monitor of the evolving composition of the magma.

In a broader study of ilmenite suites from 20 African kimberlites, Griffin et al. [10] found trends generally similar to those shown in fig. 3, but with clear differences from pipe to pipe. In general, each kimberlite appears to contain ilmenites derived from a single batch of magma, and the compositions of these magmas are

slightly different. The result has significant implications for exploration strategies; it may be possible to tell from analysis of an ilmenite concentrate how many kimberlite bodies are to be found within an exploration area. It is also an important argument in favour of a genetic relationship between the ilmenite-forming magma and the kimberlite which brought the ilmenites to the surface.

Many non-diamondiferous alkalic basalts carry magnesian ilmenites that overlap the major-element compositional range of kimberlite ilmenites, and these pose a serious exploration problem. However, preliminary studies of basaltic Mg-ilmenites suggest that they have low contents of Ni, Zr and Nb compared to kimberlitic ones, and that the interelement relationships are different as well. These results suggest that the basaltic ilmenites are formed either from different magma types, or under different *P-T* conditions, or both. A separate project is underway at HIAF to examine this problem.

3.3. Chromites

Chrome spinels ((Fe, Mg)(Cr, Al)₂O₄) with high Cr contents (> 40%) are widely used as indicators of kimberlites or lamproites, especially in deeply weathered terrains such as Australia, where garnet and ilmenite may not survive. However, their meaning is commonly ambiguous: spinels with lower Cr content also occur in kimberlites and lamproites, and high-Cr spinels may be shed from a wide variety of non-diamondiferous rocks, including peridotite bodies, greenstones and gabbros.

Chromites contain relatively few trace elements that can be analyzed by PIXE; Ni, Zn and Ga are the most

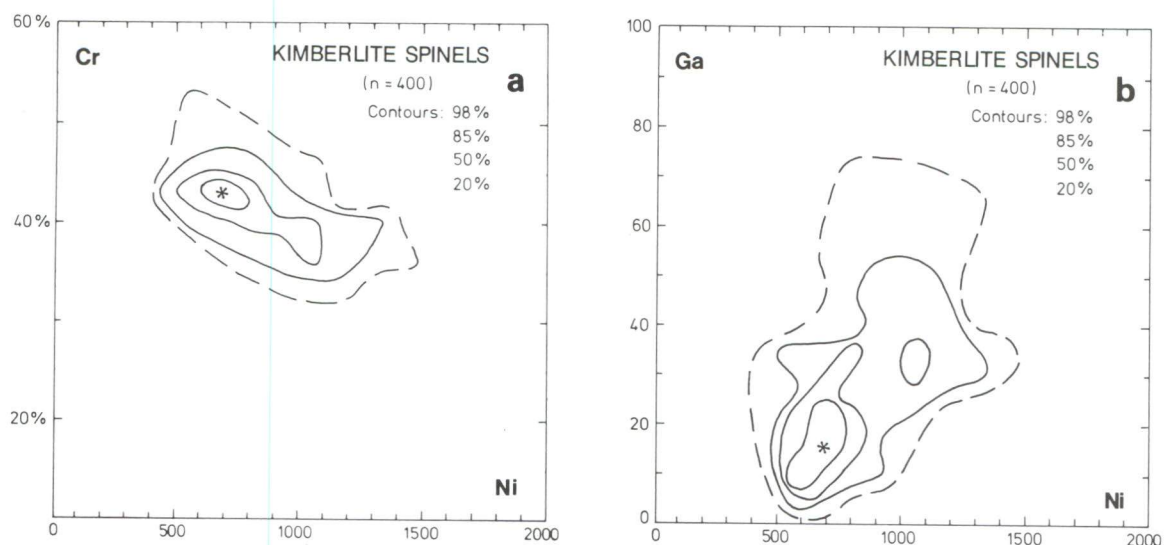


Fig. 4. Distribution of Cr, Ni and Ga in 400 chromites from African kimberlites. Dashed contour encloses 98% of data points; other contours are 85%, 50%, 20%. (Griffin and Gurney, unpublished data.)

abundant. However, when combined with the major-element data from the electron microprobe, these elements can provide useful discriminants. The compositional range of kimberlite chromites has been defined through analysis of more than 400 samples (fig. 4). While spinels from other sources may also lie within this range for individual element pairs, their interelement relations are typically different. Multivariate analysis of this database will ultimately provide a screening procedure for classification of individual grains from exploration samples.

3.4. Element partitioning

Data on trace-element partitioning between coexisting phases are potentially of great importance not only in geothermobarometry [7], but in testing for equilibrium, modelling of partial melting and fractional crystallization, and understanding of metasomatism in the mantle. Griffin et al. [1,11,12] have analyzed the effects of pressure, temperature and composition on partitioning of trace elements between phases of eclogites and peridotites. O'Reilly et al. [13] have studied the distribution of trace elements between the minerals of metasomatized spinel peridotite xenoliths, and demonstrated the importance of crystal chemistry in controlling the trace-element composition of rocks formed in open systems.

3.5. Inclusions in diamond

Mineral phases trapped during the growth of a diamond crystal are shielded from compositional change or other physical modification during the subsequent

history of the diamond; they carry important information on the environment and processes of diamond formation. These inclusions can be classified into two suites, corresponding to the two major mantle rock types. The *peridotite suite* is dominated by olivine, Cr-rich garnet and Cr-rich chromite; the *eclogite suite* is dominated by sodic clinopyroxene and low-Cr, often Fe-rich, garnets.

Griffin et al. [14] used Ni thermometry to demonstrate that some peridotite-suite garnets were trapped at unusually high T ($> 1300^\circ\text{C}$), suggesting formation in thermal aureoles around deep-seated magma bodies, and possibly in the presence of melt. Most other garnet inclusions give temperatures consistent with formation at similar depths, but lower T , and thus in the solid state. They also found that the trace-element patterns of one group of low-Ca garnets requires a two-stage evolution; an overall depletion of the mantle rocks in low-melting components was followed by equilibration with a carbonate-rich melt or fluid.

A study of eclogite-suite inclusions in diamonds from the Argyle mine (Australia) provided further evidence for high formation temperatures [1]. This study also showed that several inclusions of garnet and pyroxene within single diamonds were not in compositional equilibrium when they were trapped. The results were interpreted as showing crystallization of diamond in an open system that was undergoing rapid compositional change. Moore et al. [15] showed that the trace-element compositions of eclogite-suite inclusions in Monastery Mine diamonds do not match those of minerals in eclogite xenoliths from the same mine. These data suggest that metasomatic processes have modified the compositions of mantle rocks following the crystallization of

diamond. McCandless et al. [16] showed that different varieties of diamond from the Orapa mine contain similar types of garnet inclusions.

4. Conclusion

Trace-element studies of heavy-mineral concentrates and xenolith material are providing tools for the discrimination of barren and diamondiferous source rocks, and for recognizing the presence of multiple sources within an exploration area. Studies of mantle-derived xenoliths and macrocryst suites provide information on mantle processes, including those important for diamond formation. The data are pertinent to determining the types of magmas present, and their crystallization histories; the interaction between magmas and their wall rocks; and the relationship between the "megacryst magma" and kimberlite. Especially exciting is the information on time scales which is becoming available through proton-probe studies of trace-element zoning in garnets and other phases. Studies of inclusions in diamonds are providing important information on the environment of diamond formation, and on metasomatic processes through time.

Ultimately, understanding of the mantle processes that control the formation of diamond, kimberlite and other diamondiferous rocks will lead to better exploration models for locating primary deposits of diamonds. Proton-microprobe studies are making a significant contribution to that understanding.

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Section VIII. Geological and mineralogical applications

The proton microprobe: a revolution in mineral analysis

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Application of the proton microprobe as a quantitative tool for trace-element microanalysis in the geosciences can be considered to have crossed the threshold of acceptability in a number of areas, particularly in igneous and metamorphic mineralogy and petrology. In the minerals industry, applications in base metal ore mineralogy provide new data useful for both processing and genetic studies. Applications in diamond and gold exploration are developing into new methods, with potential widespread acceptance. The paper will review a few case histories, and discuss the limitations of the current state-of-art and conditions conducive to widespread acceptance by geoscientists and by the minerals industry.

1. Introduction

The anticipated benefits of the proton microprobe applications in the geoscience have been realized in an ever increasing number of areas, marked by the progression from experimentation to routine application of the technique. Better access to accelerator facilities by geoscientists, close links between physicists and geoscientists, and dedicated facilities are requisites of this progress. Such conditions apply in a number of laboratories, notably at Heidelberg, Witwatersrand and Los Alamos [1–3]. HIAF is an example of a dedicated facility, established to enable sustained development of the applications in the geosciences, and promote the introduction of accelerator-based analytical methods into the mineral industry [4]. This includes not only the proton microprobe [5], but other ion beam analysis (IBA) methods and accelerator mass spectrometry (AMS) as well. In Australia this is warranted by the important role of the mineral industry in the national economy.

The statistical nature of geological samples and data requires analysis of large numbers of samples, and the interpretation often depends critically on the accuracy of the data. Speed of analysis governs the viability of the method, particularly in the industrial context, affecting among others the cost factor. With appropriate design of both hardware [5] and software [6] these requirements can be fulfilled successfully.

While experimentation continues, significant progress has been achieved over the past few years. In particular, quantitative analytical micro-PIXE has found

an appropriate niche in igneous mineralogy and petrology, marked by contribution to advances in the mainstream areas. In sulfide mineralogy, trace-element data have contributed to the understanding of ore genesis and found direct application in exploration and processing of base metal ores. The present paper reviews the potential and constraints of analytical micro-PIXE, and presents a few case histories for illustration.

2. The proton microprobe

The applications of the proton microprobe in general have developed along two virtually separate lines. In one the emphasis is on imaging and on the attainment of the best resolution, with the scanning mode as the main mode of operation [7,8]. The other concentrates on its use as a quantitative microanalytical tool [6,9], with resolution considered as a second priority. The latter has been the line adopted at HIAF for geoscientific applications. Progress in this has been reviewed in a number of recent papers [11–13], and is the subject of the present paper.

One emerging conclusion is that quantitative micro-PIXE in the geosciences has graduated from being an experimental tool, into a vital tool for the progress in a number of specific areas. The successes achieved thus far have been based mainly on adaptation of electron microbeam methodology, i.e. nondestructive in-situ trace-element analysis by induced X-ray spectrometry. The better sensitivity (as low as < 1 ppm) afforded by the lower bremsstrahlung revealed new information hitherto inaccessible or tedious to obtain. However, one has to be continually aware of alternative [14], and

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possible less expensive methods in choosing the proton microprobe as a viable tool.

While the proton microprobe methodology for mineralogical analysis can be considered as derivative of that of the electron microprobe, it is instructive to consider the contrast, and in many instances the complementarity of the two methods:

- *Sample size and preparation:* The effective depth of analysis is $\sim 5\text{ }\mu\text{m}$ for electron beams with energies 15–30 keV, typical for electron probes. For 2–4 MeV protons typically used in PIXE measurements, the effective depth of analysis varies between 10 and 30 μm , depending on the mineral. Smoothness of the sample surface (better than 0.2 μm polish) is important for electron-probe measurements, whereas for proton measurements this is not as critical. The larger excitation depth, however, implies that proton-microprobe analysis should be used with caution when grains less than 30 μm size are analyzed, due to possible excitation of underlying and overlapping phases. This could be avoided with thin transparent specimens, but for opaque minerals it may not be practical. Spatial resolution in the micron or submicron regime is thus not the most important criterion when ideal samples are in the 30–50 μm minimum size, unless special features such as zonation in minerals require it. On the other hand, the large excitation depth enables analysis of special samples, such as fluid inclusions [15].

- *Minimum detection limit (MDL):* The ultimate minimum detection limit is determined mainly by the presence of continuum background, primarily due to bremsstrahlung. In the case of the electron probe, this limits the detection of trace elements to levels > 500 ppm with standard energy-dispersive spectrometers (EDS, i.e. Si(Li)); 50–100 ppm is achievable with great care using wavelength-dispersive spectrometers (WDS). For protons, MDL in the 0.1–50 ppm range is achievable even with energy-dispersive spectrometers (EDS), by virtue of the lower level of background. However, this is achieved only at a certain required integrated beam charge. For example, to achieve 1 ppm MDL of transition elements in a silicate matrix, 10 μC of 3 MeV proton beam is required when the Si(Li) detector has a solid angle of 50 msr. With a 10 nA beam this requires approximately 20 min. The measurement time would be unviable if a beam current of less than 1 nA is available.

- *Beam intensities and resolution:* Electron sources are much brighter than proton sources, e.g. $10^5\text{ A}/(\text{cm}^2\text{ sr})$ compared to only about 20 for a duoplasmatron source. Hence viable electron beam currents (50–100 nA) are readily available at a resolution of around 1 μm , with aberration effects already taken into account. Even in the absence of aberrations, to achieve comparable resolution for protons, the available beam intensity would be considerably lower which may render quantitative analysis unfeasible [16]. The best beam

current reported at 1 μm resolution is 100 pA [7,8], at which point the chromatic aberration dominates. With achromatic systems [17], the resolution could be improved in principle, but in practice spherical aberration and parasitic aberrations due to imperfect construction of the lens can dominate and limit the beam currents achievable at micron resolution. At HIAF, the microprobe is based on an electrostatic “Russian” quadruplet system [5,16], a 100 pA proton beam with 3 μm resolution was achieved with a 32 μm object aperture and 0.5 mm diameter lens aperture. A practical beam current for quantitative trace-element analysis of 10 nA can be obtained with $\sim 20\text{ }\mu\text{m}$ beam spot.

- *X-ray detection:* Filters are important in PIXE measurements using and EDS. The basic function is to protect the Si(Li) detector from the scattered beam, but the more important aspect is to tailor the measurement for optimum sensitivity for desired elements by attenuation the count rate of major elements, and to reduce pileup effects. The latter could be essential in number of cases, e.g. Rb or Sr masked by pileup from Fe. Special filters can be used exploiting X-ray absorption edges, but secondary fluorescence of the filters themselves can mask elements of interest. Ability to change filters quickly is an important feature from a practical viewpoint.

The use of filters, however, also reduces the ability to measure the major element composition of most minerals. The minimum filter for 3 MeV protons absorbs most X-rays from elements below Na. For heavier beams a thinner absorber can be used, and consequently lighter elements can be detected. However, this may still require supplementing the data with that obtained the electron probe. This may also be required for other reasons, e.g. when beam integration is a problem due to charge buildup on insulating targets. A large dynamic range of beam current can cause problems in secondary methods of beam measurement.

- *Electron detection:* Backscattered electrons in electron-probe analysis are copious and provide good contrast for heavy elements in light matrices, e.g. grain noble metals on olivine grain boundaries. Most scanning electron probes are operated using this radiation. To obtain comparable data by scanning PIXE is not as advantageous: the secondary electrons are not as copious and do not give sufficient discrimination, and the X-ray yield is usually very low, and viable beam current at comparable resolution is not possible.

- *Other radiations:* The additional advantage of using proton or other ion beams is the possibility of exploiting the scattered beam and gamma-radiations. In the case of proton and alpha beams, Rutherford backscattering (RBS) or resonant scattering can be used to determine light elements e.g. C, O, N. Gamma rays from resonant and nonresonant reactions induced by protons can be used to detect an assortment of light

nuclei, e.g. fluorine. Development in this area is progressing rapidly [18], but will not be discussed further in this paper.

Conditions considered optimum for quantitative micro-PIXE of mineralogical samples can thus be summarized as follows:

- For monomineralic-grain analysis, the size is preferably greater than 30–60 μm to avoid possible overlapping grains.
- For viable measurement time, and combined with the above, it follows that proton beam resolution of the order 5–20 μm is necessary and sufficient.
- To fully exploit PIXE's advantage as a trace-element probe, the scanning ability must be used judiciously. Line scan, or selective probing would be more effective for quantitative analysis.
- From the practical point of view, the ability to view the specimen in the reflecting geometry is important, if only to enable convenient positioning of the sample tuning of the beam spot.

3. Applications

At HIAF, quantitative trace-element distribution by micro-PIXE has been applied to the study of indicator minerals used in diamond exploration, diamonds, diamond inclusions, mantle-derived xenoliths and megacrysts, sulfide minerals, sapphires, native Au and fluid inclusions. The samples can be polished thin or thick sections of the rock or ore, or concentrate prepared as grain mounts as for electron-microprobe analysis.

3.1. Igneous mineralogy and petrology

In retrospect, analyses of samples of igneous minerals, except zircons are the easiest. For most minerals, Fe is the heaviest element in the matrix and thus many geochemically important marker elements such as Ni, Zn, Ga, Ge, Rb, Sr, Zr, Y, Nb and Ta can be detected with good MDL. The rare-earth elements (REE) are equally important, but their detection, however, is at present still problematic. The L lines are totally masked by either the FeK lines or the escape peaks, and for the light REE the peak-to-background is degraded by the tail of the Fe line. The K lines can be observed free of interference, but the detection efficiency for Si(Li) detectors drops dramatically above ~ 30 keV. In apatite, using the K lines, MDL values of ~ 40 ppm for La, Ce, Pr and Nd can be obtained. With a Ge detector, the K lines can be detected more efficiently, but a continuum background due to Compton-scattered gamma rays also results in a relatively poor peak-to-background ratio. For zircons, the tail of the Zr K lines degrades the MDL of all elements below it, and

for U and Th, which are the main traces, the MDL value is ~ 20 ppm.

Partitioning of these marker elements between the magma and the crystallizing phases is sensitive to pressure (P), temperature (T) and initial composition of the parent magma, and also may be dependent on the valence of the elements being partitioned. Geochemical modelling of the evolution of magmas requires accurate knowledge of these partition coefficients. Different phases may be involved in different magmas. For example, important phases at high pressure for basaltic liquid are garnets and clinopyroxene and an important phase for intermediate or granitic magmas is amphibole. The P, T -dependence of the partition coefficients can be determined in natural systems, or in experimentally synthesized minerals produced under laboratory conditions simulating the mantle conditions. Elements occurring as major or minor elements can be measured readily both in natural and synthesized samples with electron probes. However, elements which are not readily incorporated in the lattice, i.e. incompatible elements, occur only at very low levels, usually below the detection limits of electron microprobes. Increasing the concentration to measurable levels in synthetic samples may invalidate the results due to breakdown of Henry's law. With the proton microprobe, despite the limitations discussed above, detection limits for most of the important marker elements are still in the 1–10 ppm regime, making systematic study of partition coefficients under conditions close to most natural systems possible. An example of such study of partition coefficients of Nb and Ta, thought previously to be geochemically coherent, between garnet, clinopyroxene and basaltic liquid, showed large fractionation effects which must be taken into account in geochemical modelling [19].

Changes in the melt composition due to fractional crystallization or magma mixing result in a spectacular distribution of trace elements in certain phases of natural systems, e.g. kimberlites and lamproites, the main source for diamonds. Igneous minerals contained in these rocks, sometimes as megacrysts, preserve the signature of their evolution in the upper mantle, prior to emplacement by eruption. The minerals are usually dispersed by weathering process and erosion. Of these, ilmenites, garnets and chromites are the most commonly used in diamond exploration and the characterization of the source rocks [20]. For example, fig. 1 shows the Zr content of ilmenites from one kimberlite pipe in South Africa. These show the effects of fractional crystallization, with dramatic changes in concentration marking the onset of precipitation of other phases, e.g. zircons. Similar results were obtained for Ni in chromites, where sudden changes can be attributed to the precipitation of olivine. Fig. 2 shows the result for ilmenites from a number of pipes. Dependence on the

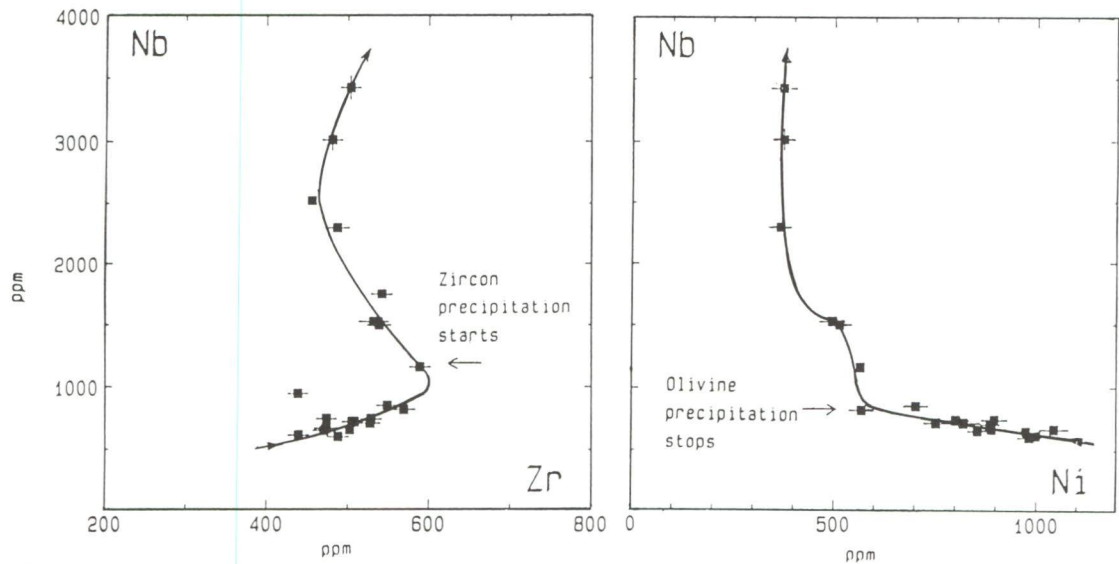


Fig. 1. Correlation diagrams of trace elements in ilmenites from one kimberlite pipe, showing the effect of fractional crystallizations. Precipitation of Zr depletes Zr in the melt, and similarly olivine depletes Ni.

initial magma composition is reflected in the grouping of the concentrations levels, whereas the trend in the individual grouping is governed by the evolution of the magma. Such grouping provides the discriminants to identify multiple sources and/or different types of rocks in diamond-exploration applications.

The effect of temperature is equally spectacular in the case of Ni in pyrope garnets coexisting with olivine [21]. Partition between the two phases, and the roughly constant Ni content of mantle olivines at around 3000 ppm, results in a single mineral geothermometer. Supplemented with the appropriate geotherm, the ther-

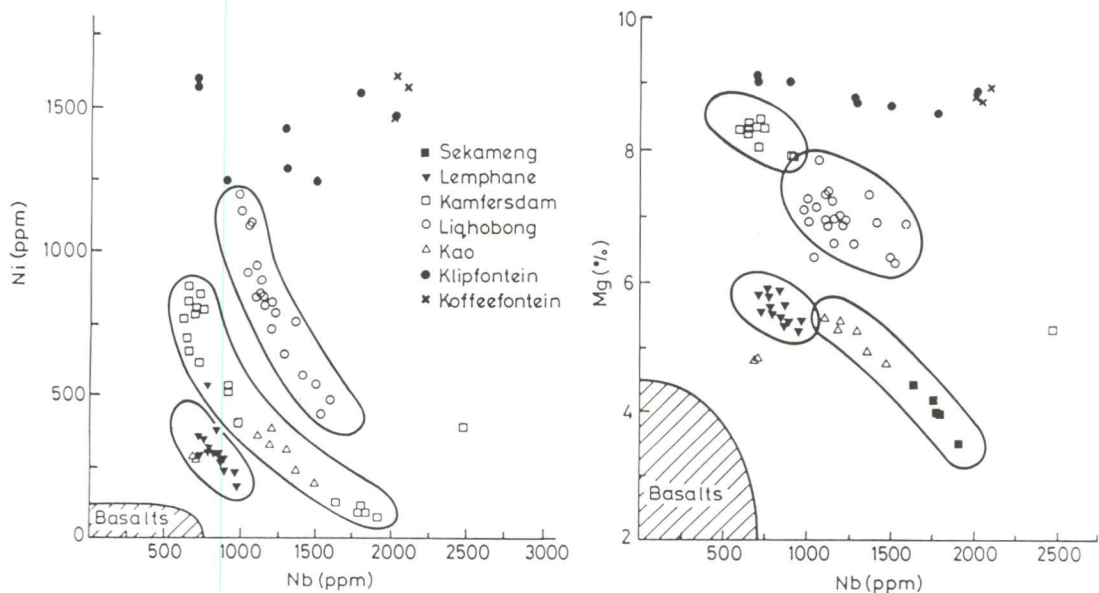


Fig. 2. Result of analysis of ilmenites from a number of pipes showing grouping of the trace-element distribution, which can be used to identify multiple sources. The trend observed in each group reflects the fractional crystallization effect. The grouping also can be used to distinguish source rocks; those from basalts are clearly well separated from those from kimberlites.

mometer can be used to assess the prospectivity of a potential diamond source.

The effect of pressure and temperature, and associated processes of deformation and metasomatic events are also reflected as compositional zoning in individual mineral grains. With the proton microprobe the effect on incompatible elements can be studied in detail. Infiltration of melts or other fluids into a rock will change the bulk composition of the system, while changes in temperature will change the partitioning of elements between minerals. Elements with appropriate diffusion rates will record these changes as zoning patterns, and it is possible to derive information on the nature of the processes and the time scales involved [22].

3.2. Sulfide mineralogy

In sulfide minerals, the trace elements may be of interest both geochemically (Se, Cd, In, Ni, Sb, Sn, Hg) and economically (Au, Ag). In arsenopyrite Sb can substitute for As, and both As and Sb can affect the precipitation of Au. In galena, the presence of Sb and Bi increases the solubility of Ag through coupled substitution, with AgBi or AgSb substituting for 2Pb [23]. The ratio of Ag to Sb and Bi can be used to deduce the temperature of equilibration, reflecting metamorphic or depositional temperature. Likewise the Se/S ratio is expected to increase with temperature of formation, with high Se associated with a hydrothermal-magmatic system, and a sedimentary system showing lower Se content. Although this correlation does not always hold, with the proton microprobe it is now possible to study the behaviour of Se and the other trace elements under different depositional conditions systematically. The temperature dependence is normally obtained from isotopic studies (e.g. ^{34}S), but if it can be obtained nondestructively from trace element analysis it would be useful as supplementary data, e.g. in the applications of the sphalerite geobarometer [24]. In general, the problem of solid solution of e.g. Fe in sphalerite, or Zn in chalcopyrite can be delineated through systematic studies of natural and synthetic samples [9,25]. Detection limits with EDS detectors are typically in the range 5–20 ppm for most of the elements of interest. For galena, MDL values are generally higher, and Hg and Bi can only be detected with a MDL value at around 200 ppm due to severe interference problems.

From the point of view of mineral processing, the distribution of Ag among coexisting sulfides is of economic interest [12,26]. The detailed distribution of Ag in sulfide concentrates can be used to improve beneficiation efficiency, by recovering from minor Ag bearing phases which otherwise would be lost to the tailings. In these phases, except for those containing high level of Sb, e.g. tetrahedrite or stibnite, Ag readily can be determined to 1–10 ppm.

Arsenopyrite, pyrite and pyrrhotite are usually the phase carrying Au either as submicroscopic particles or in complete solid solution. Ore containing Au in such phases is known as refractory ore, and requires roasting prior to the usual processing. Detailed distribution is therefore required to determine whether the ore is worth processing. In pyrite and pyrrhotite, MDL of 5 ppm can be obtained, while in arsenopyrite the tail of As degrades the MDL to ~40 ppm. While the absorber can play an important role in enhancing MDL by absorbing the major lines, this does not help the Au in the arsenopyrite case.

Sulfide phases can also be carriers of the other noble metals, the platinum group elements (PGE). These elements occur at very low crustal abundances, but are obtained economically from placers, komatiite-hosted Ni–Cu ores and layered mafic/ultramafic intrusions. Cabri et al. [9] have studied the distribution of PGE in the Sudbury Ni–Cu deposit and the Stillwater layered complex. Another example of a layered intrusion is the Merensky Reef in the Bushveld Complex intrusion of South Africa, one of the main sources of PGE. In this deposit, the PGEs occur mainly as platinum group minerals (PGM) in sulfide-bearing gabbros associated with the chromitite layers. A significant fraction of the PGE is contained in the sulfides and a study of the detailed distribution in them using the proton microprobe revealed pyrrhotite and pentlandite as significant carriers. MDL values of 1.5–2 ppm are obtained for Pd, Rh and Ru, and 5–7 ppm for Pt, Os and Ir in these minerals [28]. In addition to the direct application of micro-PIXE, a supplementary method combining it with a preconcentration step by fire assay can be used to determine the bulk concentration of Pt and Pd. A detection sensitivity of 6 ppb, comparable to crustal abundances, can be obtained by analyzing the silver prills from the Pb–Ag fire assay [29,12].

3.3. Trace elements in gold

Silver is nearly always present in native Au, and the variation of its content can be associated with different genetic types and interpreted as the effect of temperature of formation and salinity of the ore fluids [30]. However, the Ag/Au content can be altered during fluvial transport which can obscure the genetic information. The presence of other trace elements, e.g. Fe, Cu, Zn, Pb and Hg was demonstrated by Warren and Thompson [31] by spectrographic techniques. They concluded that observed trace-element variations are controlled mainly by the characteristics of the metallogenic provinces rather than the type of deposit, raising the possibility of using trace elements as a more sensitive discriminant. This would have implications in exploration where study of alluvial gold grains can be used to establish their provenance through genetic associations

and to identify multiple sources. The early spectrographic studies were beset by problems of contamination due e.g. to mineral inclusions and multiple sources could not possibly be identified because a large number of grains were required for each analysis. Later electron-probe studies avoided these problems, enabling one to distinguish traces in solid solution, but most of these are below detection limits [32].

In a preliminary study of trace element in gold, a suite of samples from a number of sources in Tasmania have been analyzed using micro-PIXE at HIAF [33]. Fig. 3 shows a typical spectrum obtained from the gold grains, showing the dominant Au and Ag peaks. This example illustrates the limits of the EDS system: the Au L lines masked most of the L lines for adjacent elements. Pb and Bi can only be observed reliably through their L gamma lines. The PGE L lines are also unresolved, and this problem is further compounded by "tails" of the Au L photopeaks at the low-energy side which can be time dependent. Hg, with peaks higher in energy than Au, can be fitted unambiguously, but the MDL is still in the 200 ppm regime. The tails of the Ag K lines interfere with the detection of Pd. More significantly, Pd is also interfered with by the pileup peaks from Au, as can be seen in fig. 3. Despite these limitations, the preliminary results are encouraging. In these samples the Au ranges from 69 to 98 wt.%, and Ag from 1.4 to 30 wt.%. Elements observed include Hg, Bi and Cu at about 0.1% concentrations, and other base metals (Fe, Pb and Zn) at < 0.1%. Traces of Pd, As and Mn were also measured. The Mn numbers are unreliable because of the high absorption by the filter used.

Examples of the results obtained for Cu and Hg are shown in the correlation diagrams in fig. 4. The data obtained so far showed some evidence of characteristic differences between different deposit types and styles of mineralization, between deposits of the same type and between different mineralogical associations within a particular deposit. High Hg content was observed for mafic/ultramafic associations. Alluvial samples show decreasing Ag content with distance from the source. With more analysis, more definite characteristics may emerge.

4. Conclusion

The examples discussed here and elsewhere in the Proceedings demonstrate that the application of the proton microprobe in mineralogy is truly revolutionary in the sense that it provides new or much better-quality data which can provide much tighter constraints on geological interpretations. The applications illustrate the exploitation of various aspects of quantitative micro-PIXE: the sensitivity, rapidity of analysis, large effective depth of analysis (fluid inclusions), and wherever necessary, the spatial resolution (zoning in minerals). The tradeoff between spatial resolution and beam intensity is one area where development in lens and ion-source technology can make significant improvements. Within the present constraints, further improvements in detector technologies, e.g. large-area and/or multiple-detector systems, can improve efficiency. This and other features such as a quick sample changer, a good

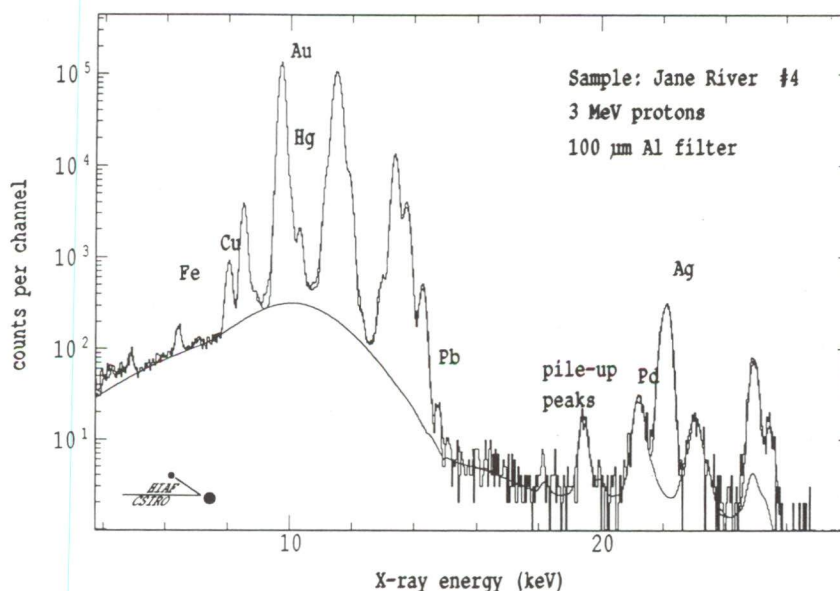


Fig. 3. A typical spectrum obtained from the gold grain, showing the dominant Au and Ag peaks, and the fitted spectrum with the pileup peaks indicated.

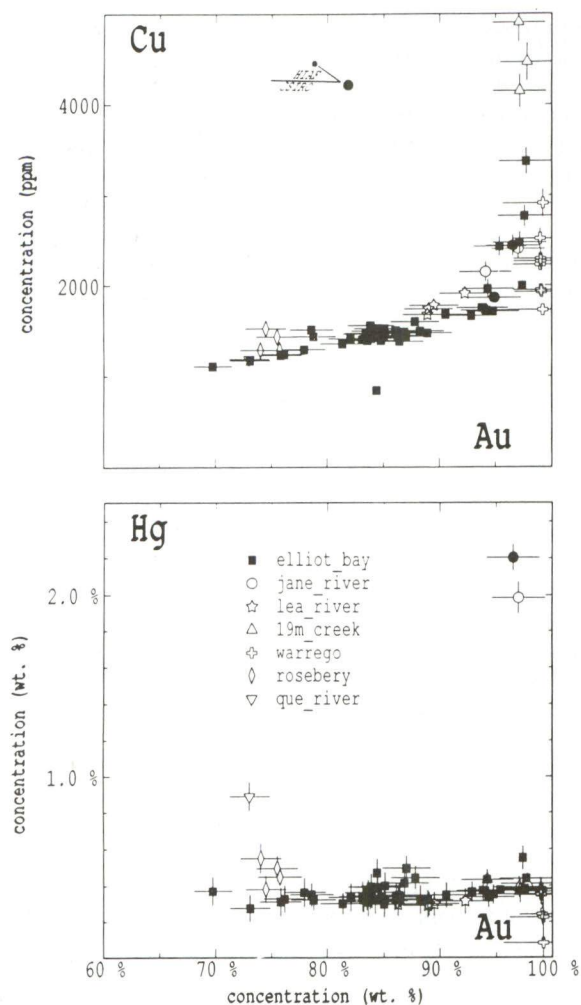


Fig. 4. Correlation diagram for Cu (in ppm) and Hg(%) vs Au(%) for the samples studied. With more data, discrimination between different types of sources will become more evident.

sample-viewing system, and last but not least an efficient data handling system would reduce unit cost of analysis, which is one of the crucial factors for widespread acceptance by the minerals industry.

The wavelength-dispersive spectrometer (WDS) promises resolution of some currently intractable problems. This can be due either to interference problems (detection of REE or of Au/As/Pb/Bi/Hg and photopeak tailing problems in Pd/Ag) or to generally poorer peak-to-background in analysis of high-Z minerals such as zircons and uraninite. The last limitation also holds true for the detection of trace elements lighter than Fe. However, the use of a WDS may be hampered by insufficient beam currents, when high spatial resolution is also desired.

The present review covers one perspective of the use of the proton microprobe in mineralogical applications.

As more geoscientists discover the instrument, the scope and mode of applications will also grow, and ultimately the instrument should be regarded as a standard, vital and versatile tool for advances in the geosciences. However, one has to be continually aware of parallel development of competing methods such as the ion microprobe, the synchrotron radiation microprobe, and also the electron microprobe which is being improved steadily. It is equally important to recognize the appropriate niches for the various techniques in order to capitalize on their respective unique features.

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An AMS facility for minerals exploration research

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An AMS (accelerator mass spectrometry) system based on a Tandatron has been constructed at the CSIRO HIAF laboratory at North Ryde, and is currently undergoing tests. The system is designed to enable cosmogenic isotope based chronology, and eventually will be developed to enable ultratrace measurements in mineralogical samples.

1. Introduction

HIAF is an analytical laboratory based on a model 1430 Tandatron accelerator, commissioned in late 1983 [1]. It is dedicated to developing IBA (ion beam analysis) and AMS applications in the geosciences in support of the Australian minerals industry. An essential requirement for mineralogical and petrological applications of IBA is the development of the proton microprobe, completed in 1985, to enable in situ microanalysis of monomineralic grains, the fundamental constituent of geological samples [2,3]. With this instrument, significant progress has been achieved in the area of trace element geochemistry, particularly in igneous mineralogy leading to new methods of exploration.

The development of AMS was carried out mainly in recognition of its importance in geochronology, based on cosmogenic light radioisotopes. The research interest of the Division lies mainly in the applications of ^{10}Be and ^{36}Cl dating to problems relevant to exploration and mining. The scope of published work on applications of ^{10}Be [4], ranging from soil transport and erosion studies, rock exposure ages on to petroleum dating offers exciting prospects in research of ore and petroleum genesis as aids in exploration. Similarly, the information from ^{36}Cl as a tracer and chronometer of groundwater can be an important supplement in hydrogeochemical methods of exploration, and water management in arid areas. In addition to the direct requirements in the minerals industry, HIAF is accessible by other areas of research, and thus the AMS facility will also be available for ^{14}C dating.

Of more direct interest to minerals research is the AMS capability to detect very low levels (ppb) of trace elements. So far the method has been applied using a submillimeter sputtering beam, which is not adequate for most measurements requiring monomineralic in situ microanalysis [5]. A microprobing sputter source must be developed for successful applications of AMS as a trace analyzer.

2. The AMS system

The HIAF-AMS project will proceed in two stages, with the first resulting in standard AMS capability, viz. ^{10}Be , ^{14}C dating on "bulk" samples. ^{36}Cl detection will also be attempted. The second stage involves the development of the microprobing Cs sputter source. The AMS system incorporates the existing beam transport system at HIAF, with the addition of a beamline for the detection system, and a separate injector.

A schematic of the HIAF beam transport system, including the AMS system, is shown in fig. 1. The AMS injector system is based on a double focusing, 90° analyzing magnet with a radius of 30 cm and beam product (ME/q^2 in amu MeV/e² units) of 7, with a maximum, aberration-limited momentum resolution of 6500 for an object diameter of 0.25 mm. For normal operation using typical ion sources, a more moderate resolution is expected for good transmission efficiency through the accelerator. The magnet box is electrically insulated from the rest of the beamline to permit energy modulation of the incident beam ("bouncing") to maintain the same magnetic rigidity. A 90° electrostatic spherical analyzer with 75 cm radius preceding the magnet will be added in the future, to improve the rejection ratio of adjacent isotopes.

The beam from a General Ionex model 834 Hiconex sputter source is focused by an einzel lens to form a waist at the magnet's object slits. The beam is further transported to the original low-energy cup through the "old", demagnetized injector, by means of another einzel lens. Distances are chosen to match the emittance of the AMS injector system to the acceptance of the original system. The "cone" of the Hiconex source, which holds the sample to be sputtered, is modified to permit focusing of the Cs beam onto the downstream side, and into a smaller area. The sample is loaded into a "well" in the cone (1 mm diameter and 1 mm deep). This modification reduces the amount of sample required and improves the source emittance.

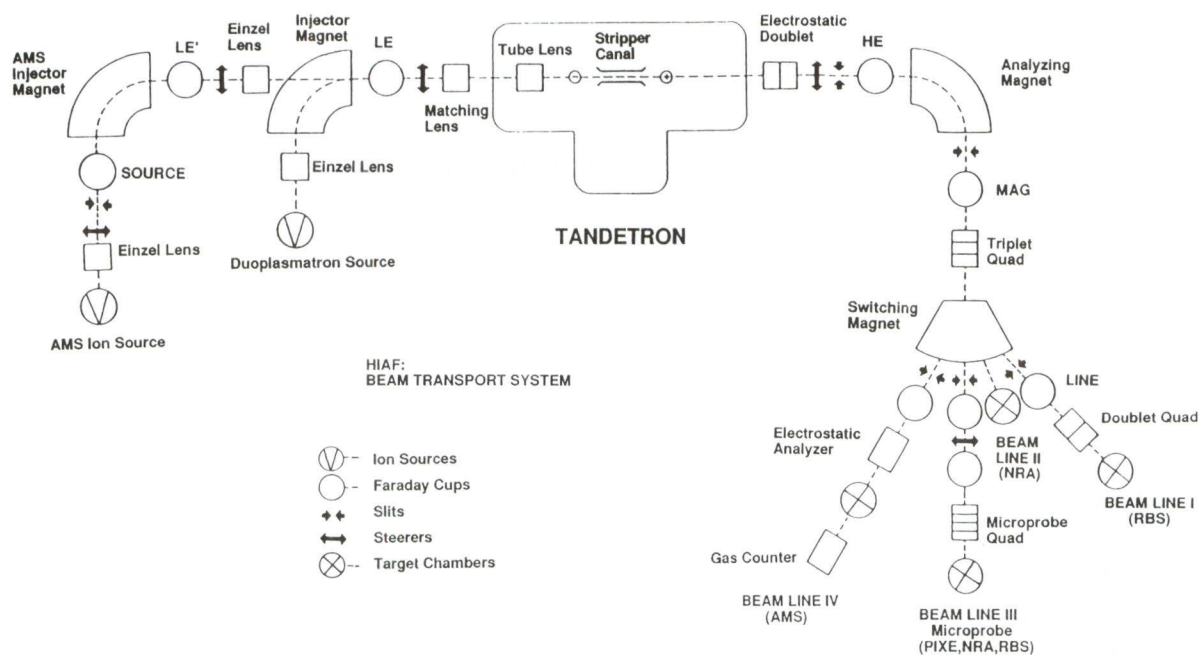


Fig. 1. A schematic of the HIAF beam transport system, showing the AMS system comprising the AMS injector and the AMS beam line. The electrostatic analyzer bends the beam downwards by 12° into the gas counter.

The beam passes through the usual two stages of acceleration with gas stripping at the terminal. There is currently no terminal pumping, which some believe to be critical for reducing the effect of fractionation through the accelerator, but there is provision for its installation. After the acceleration the beam is analyzed by the 90° analyzing magnet (beam product = 16 amu MeV/e²). The more abundant isotopes are measured in the Faraday cup at the image point of this magnet. A multi-Faraday cup system with four independently adjustable cups has been designed and will be implemented as part of the second stage development. This will allow detection of the abundant isotopes without the need to alter the analyzing magnet setting. In the present system, the analyzing magnet has to be adjusted for measurements of each isotope. To facilitate such switching, a computer controlled beam transport is being implemented, which will permit automation of the operation. The present magnet is inadequate for detection of heavy isotopes ($A > 60$) at moderate terminal voltages (~ 1 MV). For the second stage development, where detection of elements up to U is anticipated, a new magnet with a much higher beam product will be acquired.

The rare isotope is further focused by the magnetic triplet into the detector beam line through a 22.5° deflection using the switching magnet. A 12° electrostatic spherical analyzer with 4 m radius and 11 mm gap feeds the beam into a gas proportional counter. The

counter is a conventional counter with a Frisch grid, operated with isobutane at pressures in the 10–40 mbar range. The anode is segmented into three parts, each 5 cm long. The gap between the cathode plate and the grid is 25 mm, bisected by the counter window axis. Initial tests were carried out with a 6 mm diameter window made out of multiple layers of thin films of VYNS, capable of withstanding up to 200 mbar pressure difference. For ^{12}C beam, this was eventually enlarged to 10 mm diameter using a $2.5\ \mu\text{m}$ mylar film, to achieve 100% transmission efficiency to the detector. Alignment of the counter chamber and adjustment of focus were carried out using a ^{12}C beam as a pilot beam monitored using strongly fluorescing willemite (Zn_2SiO_4) screens at selected points, including that in front of the window.

3. Test and progress

3.1. The source

Tests were carried out on the modified Hiconex cones using natural graphite and graphitized carbon, prepared by the usual method of CO_2 reduction (supplied by F. Leaney, CSIRO Division of Water Resources, Adelaide and by R. Gillespie, ANU, Canberra). With the source mounted on the original injector, analyzed beams of ^{12}C between 1 and 3 μA have been

obtained, to be compared with $\sim 6 \mu\text{A}$ typically obtained from an unmodified cone. The lower intensities in the reflected cone are to be expected considering that they are sputtered from less material. Another factor is the possibility of slight misalignment of the Cs gun in the source. It was found that when the well in the modified cone is enlarged into a slot (3 mm by 1 mm), an improved yield is obtained when the slot is in the radial direction, implying that the reflected Cs beam is slightly off axis. The source output however was found to be stable to better than 1% over periods as long as an hour.

Initial tests to produce BeO^- from oxide powder gave poor yield ($< 100 \text{ nA}$). The sample was prepared from natural BeO mixed with fairly coarse Cu powder (100 mesh). Further tests will be conducted with finer powder to improve the heat and electrical conductivity of the mixture.

In the new injector, the source yield (past the injector magnet) is considerably lower due most likely to alignment problems of the magnet. This problem is currently being rectified. Progress within the past few months has been hampered by two successive failures of the Cs gun; a new gun has been installed recently and the test is continuing.

The ^{12}C beam transmission through the accelerator was tested at 1.8 and 2.33 MV on the terminal. Analysis of the $3+$ state indicates a particle efficiency of 10% and 19% respectively, to be compared with a maximum theoretical limit of $\sim 50\%$ [6]. Most of the losses are due to the narrow stripper canal, and misalignment of

the entrance and exit. The increased efficiency with terminal voltage may reflect better matching of the injected beam emittance with the accelerator acceptance, as well as stripping efficiency. The observed efficiency compares favourably with that obtained by similar machines, e.g. 20% reported by the Arizona group [7]. Improvements are expected with further adjustments in the injector alignment.

3.2. The detector

Test with 6 and 8 MeV beams of ^{12}C , ^{16}O ($q = 3+$) and ^{28}Si ($q = 4+$) have been carried out and resolutions of 120, 150 and 220 keV were obtained for the dE anode signal. The results are consistent with a 100 keV electronic resolution, with the remainder accountable in terms of the loss distribution width. The straggling effect introduced by the change from VYNS to the thicker Mylar window contributes only an additional 5 keV to the total resolution. The obtained resolution is more than adequate to separate the C isotopes. Fig. 2 shows the spectra from the third anode at 20 mbar gas pressure, obtained with the source mounted in the old injector. The $^{14}\text{C}/^{12}\text{C}$ peak area ratio is about 25 for the modern sample (ANU sucrose). The ^{13}C intensity is high, reflecting the poor resolution of the old injector magnet. This is expected to be reduced with the new injector. For ^{10}Be measurements the energy resolution of the counter is also more than adequate, but for ^{36}Cl it is inadequate to discriminate against ^{36}S , especially due to the large energy straggling effect in the counter.

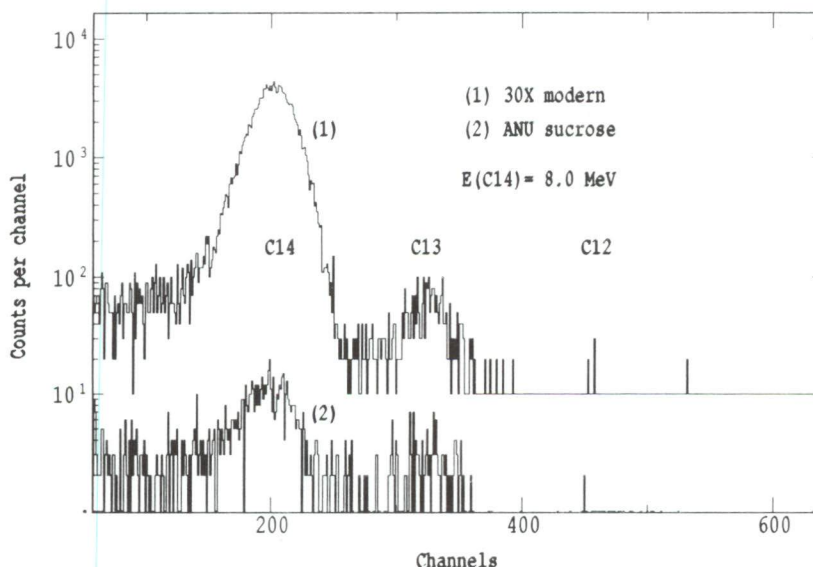


Fig. 2. Spectra from the third anode segment in the gas proportional counter obtained with the source mounted in the old injector. The samples were 30 $\times$ modern sample and ANU sucrose. The ^{14}C , ^{13}C and ^{12}C are well resolved. The poor resolution of this injector is reflected in the relatively high level of ^{13}C .

4. Summary

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References

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An AMS facility for minerals exploration research

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An AMS (accelerator mass spectrometry) system based on a Tandetron has been constructed at the CSIRO HIAF laboratory at North Ryde, and is currently undergoing tests. The system is designed to enable cosmogenic isotope based chronology, and eventually will be developed to enable ultratrace measurements in mineralogical samples.

1. Introduction

HIAF is an analytical laboratory based on a model 1430 Tandetron accelerator, commissioned in late 1983 [1]. It is dedicated to developing IBA (ion beam analysis) and AMS applications in the geosciences in support of the Australian minerals industry. An essential requirement for mineralogical and petrological applications of IBA is the development of the proton microprobe, completed in 1985, to enable in situ microanalysis of monomineralic grains, the fundamental constituent of geological samples [2,3]. With this instrument, significant progress has been achieved in the area of trace element geochemistry, particularly in igneous mineralogy leading to new methods of exploration.

The development of AMS was carried out mainly in recognition of its importance in geochronology, based on cosmogenic light radioisotopes. The research interest of the Division lies mainly in the applications of ^{10}Be and ^{36}Cl dating to problems relevant to exploration and mining. The scope of published work on applications of ^{10}Be [4], ranging from soil transport and erosion studies, rock exposure ages on to petroleum dating offers exciting prospects in research of ore and petroleum genesis as aids in exploration. Similarly, the information from ^{36}Cl as a tracer and chronometer of groundwater can be an important supplement in hydrogeochemical methods of exploration, and water management in arid areas. In addition to the direct requirements in the minerals industry, HIAF is accessible by other areas of research, and thus the AMS facility will also be available for ^{14}C dating.

Of more direct interest to minerals research is the AMS capability to detect very low levels (ppb) of trace elements. So far the method has been applied using a submillimeter sputtering beam, which is not adequate for most measurements requiring monomineralic in situ microanalysis [5]. A microprobing sputter source must be developed for successful applications of AMS as a trace analyzer.

2. The AMS system

The HIAF-AMS project will proceed in two stages, with the first resulting in standard AMS capability, viz. ^{10}Be , ^{14}C dating on "bulk" samples. ^{36}Cl detection will also be attempted. The second stage involves the development of the microprobing Cs sputter source. The AMS system incorporates the existing beam transport system at HIAF, with the addition of a beamline for the detection system, and a separate injector.

A schematic of the HIAF beam transport system, including the AMS system, is shown in fig. 1. The AMS injector system is based on a double focusing, 90° analyzing magnet with a radius of 30 cm and beam product (ME/q^2 in amu MeV/e² units) of 7, with a maximum, aberration-limited momentum resolution of 6500 for an object diameter of 0.25 mm. For normal operation using typical ion sources, a more moderate resolution is expected for good transmission efficiency through the accelerator. The magnet box is electrically insulated from the rest of the beamline to permit energy modulation of the incident beam ("bouncing") to maintain the same magnetic rigidity. A 90° electrostatic spherical analyzer with 75 cm radius preceding the magnet will be added in the future, to improve the rejection ratio of adjacent isotopes.

The beam from a General Ionex model 834 Hiconex sputter source is focused by an einzel lens to form a waist at the magnet's object slits. The beam is further transported to the original low-energy cup through the "old", demagnetized injector, by means of another einzel lens. Distances are chosen to match the emittance of the AMS injector system to the acceptance of the original system. The "cone" of the Hiconex source, which holds the sample to be sputtered, is modified to permit focusing of the Cs beam onto the downstream side, and into a smaller area. The sample is loaded into a "well" in the cone (1 mm diameter and 1 mm deep). This modification reduces the amount of sample required and improves the source emittance.

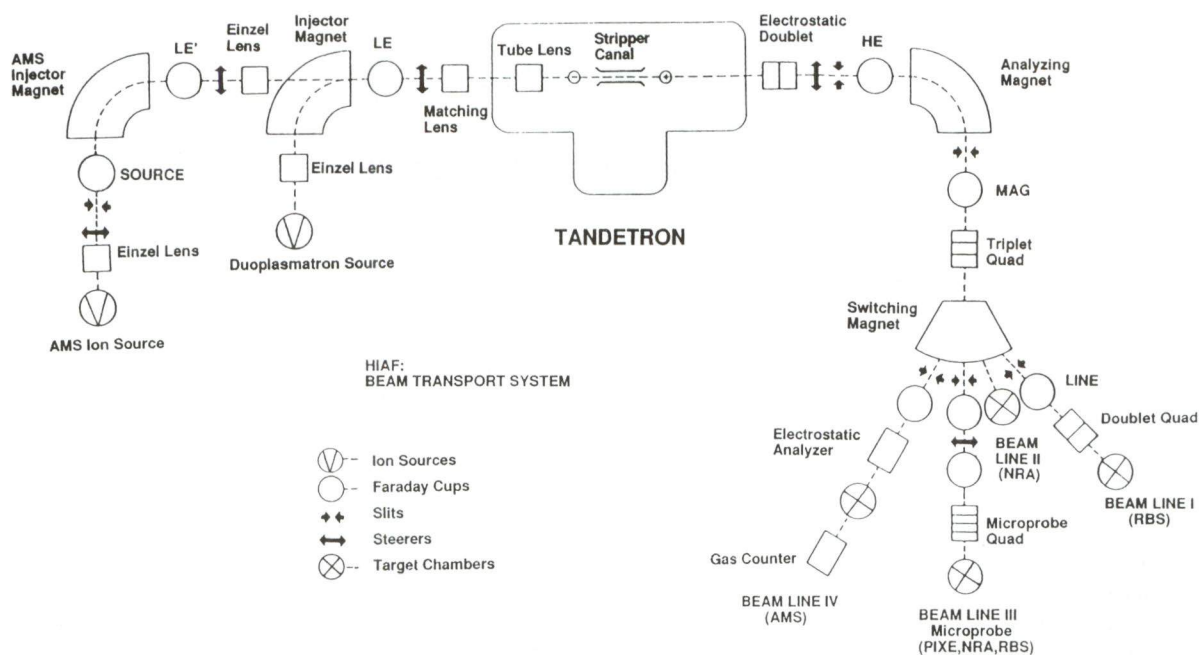


Fig. 1. A schematic of the HIAF beam transport system, showing the AMS system comprising the AMS injector and the AMS beam line. The electrostatic analyzer bends the beam downwards by 12° into the gas counter.

The beam passes through the usual two stages of acceleration with gas stripping at the terminal. There is currently no terminal pumping, which some believe to be critical for reducing the effect of fractionation through the accelerator, but there is provision for its installation. After the acceleration the beam is analyzed by the 90° analyzing magnet (beam product = 16 amu MeV/e²). The more abundant isotopes are measured in the Faraday cup at the image point of this magnet. A multi-Faraday cup system with four independently adjustable cups has been designed and will be implemented as part of the second stage development. This will allow detection of the abundant isotopes without the need to alter the analyzing magnet setting. In the present system, the analyzing magnet has to be adjusted for measurements of each isotope. To facilitate such switching, a computer controlled beam transport is being implemented, which will permit automation of the operation. The present magnet is inadequate for detection of heavy isotopes ($A > 60$) at moderate terminal voltages (~ 1 MV). For the second stage development, where detection of elements up to U is anticipated, a new magnet with a much higher beam product will be acquired.

The rare isotope is further focused by the magnetic triplet into the detector beam line through a 22.5° deflection using the switching magnet. A 12° electrostatic spherical analyzer with 4 m radius and 11 mm gap feeds the beam into a gas proportional counter. The

counter is a conventional counter with a Frisch grid, operated with isobutane at pressures in the 10–40 mbar range. The anode is segmented into three parts, each 5 cm long. The gap between the cathode plate and the grid is 25 mm, bisected by the counter window axis. Initial tests were carried out with a 6 mm diameter window made out of multiple layers of thin films of VYNS, capable of withstanding up to 200 mbar pressure difference. For ^{12}C beam, this was eventually enlarged to 10 mm diameter using a $2.5\ \mu\text{m}$ mylar film, to achieve 100% transmission efficiency to the detector. Alignment of the counter chamber and adjustment of focus were carried out using a ^{12}C beam as a pilot beam monitored using strongly fluorescing willemite (Zn_2SiO_4) screens at selected points, including that in front of the window.

3. Test and progress

3.1. The source

Tests were carried out on the modified Hiconex cones using natural graphite and graphitized carbon, prepared by the usual method of CO_2 reduction (supplied by F. Leaney, CSIRO Division of Water Resources, Adelaide and by R. Gillespie, ANU, Canberra). With the source mounted on the original injector, analyzed beams of ^{12}C between 1 and 3 μA have been

obtained, to be compared with $\sim 6 \mu\text{A}$ typically obtained from an unmodified cone. The lower intensities in the reflected cone are to be expected considering that they are sputtered from less material. Another factor is the possibility of slight misalignment of the Cs gun in the source. It was found that when the well in the modified cone is enlarged into a slot (3 mm by 1 mm), an improved yield is obtained when the slot is in the radial direction, implying that the reflected Cs beam is slightly off axis. The source output however was found to be stable to better than 1% over periods as long as an hour.

Initial tests to produce BeO^- from oxide powder gave poor yield ($< 100 \text{ nA}$). The sample was prepared from natural BeO mixed with fairly coarse Cu powder (100 mesh). Further tests will be conducted with finer powder to improve the heat and electrical conductivity of the mixture.

In the new injector, the source yield (past the injector magnet) is considerably lower due most likely to alignment problems of the magnet. This problem is currently being rectified. Progress within the past few months has been hampered by two successive failures of the Cs gun; a new gun has been installed recently and the test is continuing.

The ^{12}C beam transmission through the accelerator was tested at 1.8 and 2.33 MV on the terminal. Analysis of the $3+$ state indicates a particle efficiency of 10% and 19% respectively, to be compared with a maximum theoretical limit of $\sim 50\%$ [6]. Most of the losses are due to the narrow stripper canal, and misalignment of

the entrance and exit. The increased efficiency with terminal voltage may reflect better matching of the injected beam emittance with the accelerator acceptance, as well as stripping efficiency. The observed efficiency compares favourably with that obtained by similar machines, e.g. 20% reported by the Arizona group [7]. Improvements are expected with further adjustments in the injector alignment.

3.2. The dectector

Test with 6 and 8 MeV beams of ^{12}C , ^{16}O ($q = 3+$) and ^{28}Si ($q = 4+$) have been carried out and resolutions of 120, 150 and 220 keV were obtained for the dE anode signal. The results are consistent with a 100 keV electronic resolution, with the remainder accountable in terms of the loss distribution width. The straggling effect introduced by the change from VYNS to the thicker Mylar window contributes only an additional 5 keV to the total resolution. The obtained resolution is more than adequate to separate the C isotopes. Fig. 2 shows the spectra from the third anode at 20 mbar gas pressure, obtained with the source mounted in the old injector. The $^{14}\text{C}/^{12}\text{C}$ peak area ratio is about 25 for the modern sample (ANU sucrose). The ^{13}C intensity is high, reflecting the poor resolution of the old injector magnet. This is expected to be reduced with the new injector. For ^{10}Be measurements the energy resolution of the counter is also more than adequate, but for ^{36}Cl it is inadequate to discriminate against ^{36}S , especially due to the large energy straggling effect in the counter.

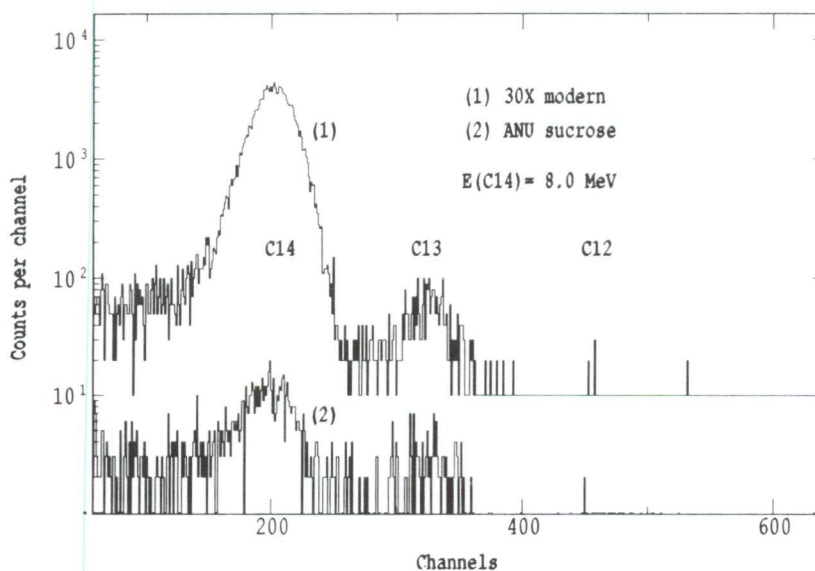


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MICRO-PIXE (PARTICLE-INDUCED X-RAY EMISSION ANALYSIS) APPLICATIONS IN MINERALS RESEARCH

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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 $\sqrt{2B}$. 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

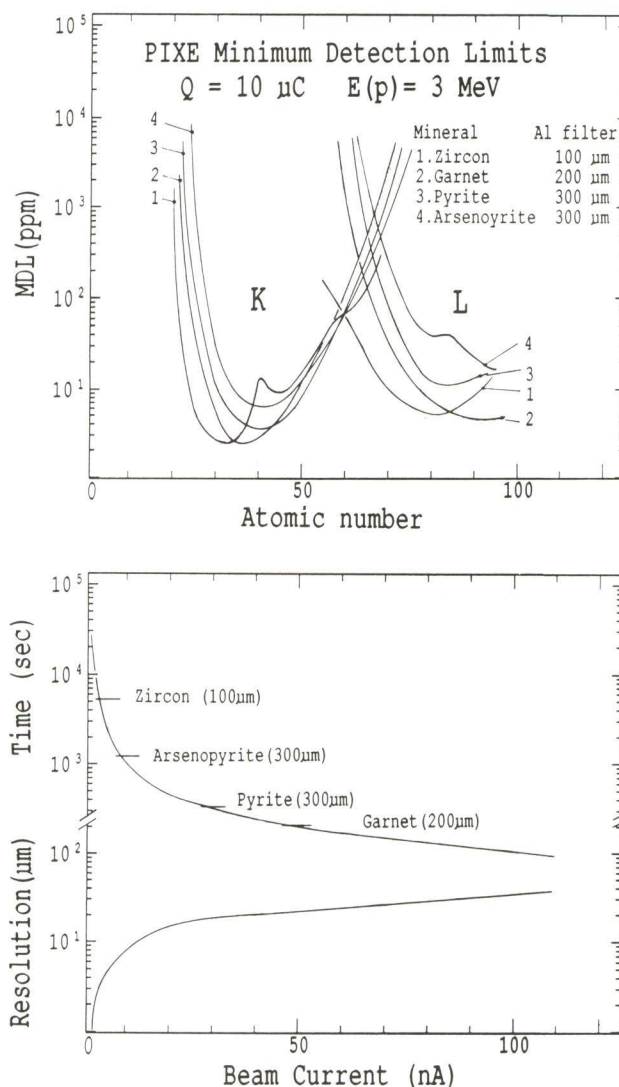


Figure 1. The top figure shows the minimum detection limits (MDL) defined at 99% confidence level for various elements in a number of minerals, detected either through their K lines or their L lines, for 3 MeV proton energy and 10 microCoulomb beam charge. The Si(Li) detector subtends a solid angle of 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 $5\text{--}30 \mu\text{m}$ 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-pyropes 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

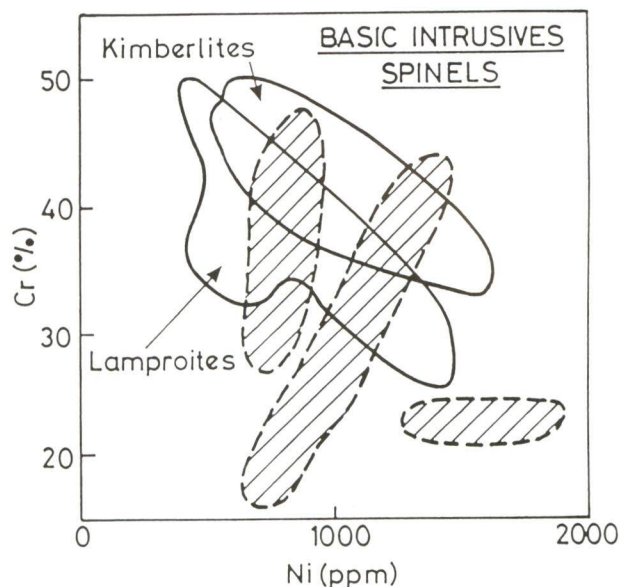


Figure 2. Correlation diagram of the distribution of trace element Ni plotted against the major element Cr from chromites (Cr-spinel) show grouping according to the source rock types. The shaded groups belonging to various barren igneous rocks (gabbros, greenstone) show different trend to kimberlites 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

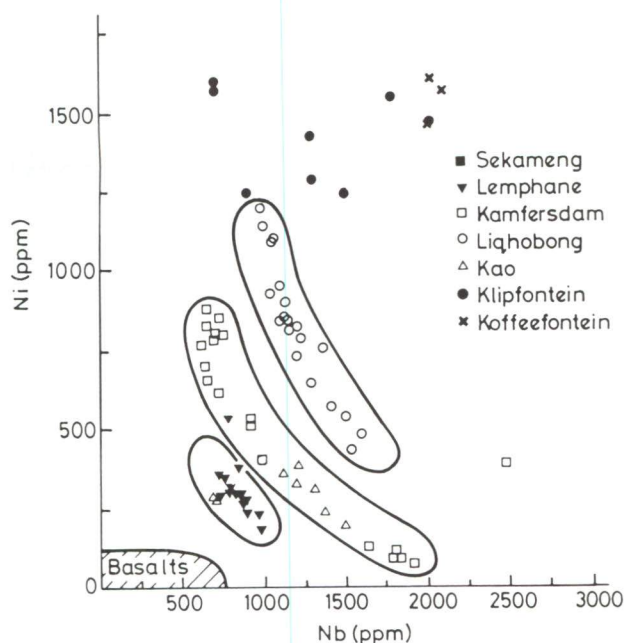


Figure 3. Distribution of trace elements Ni, Nb in ilmenites from various kimberlite pipes show groupings which can be used to identify multiple sources. The grouping represents the variation in the parent magma, while the trend in the group reflects the effects of fractional crystallization during the 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

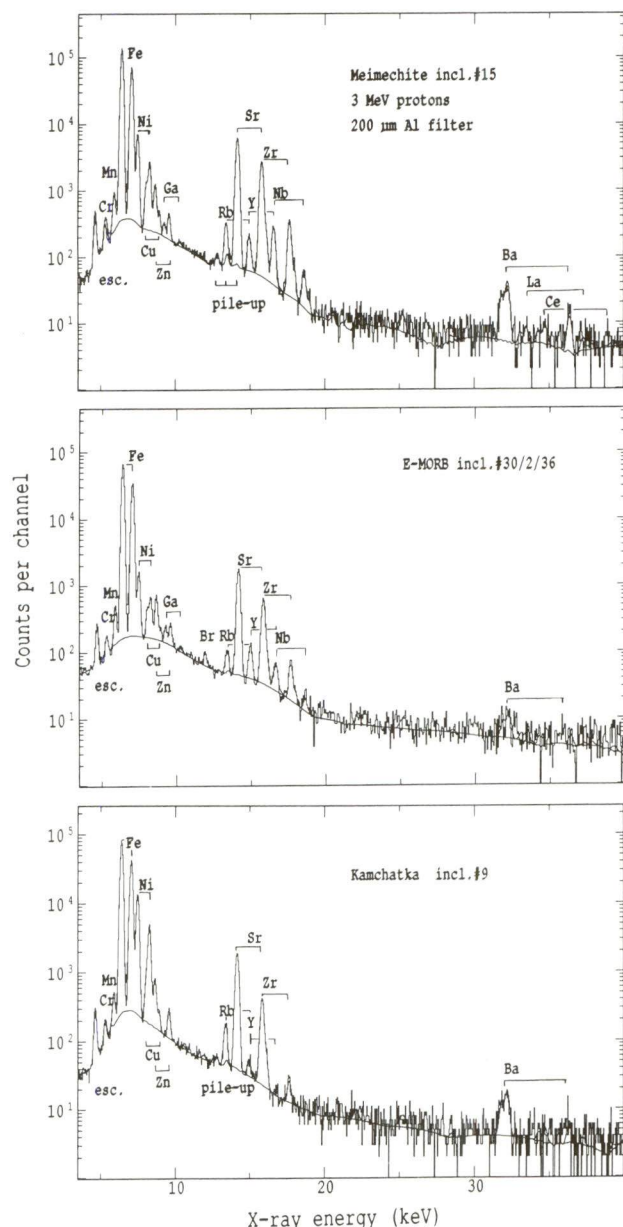


Figure 4. Spectra from melt inclusions in olivine from ultramafic rocks from different tectonic settings: continental lithosphere (top), mid-ocean rifts (middle) and subducted zone (bottom). The trace elements of interest are Rb, Sr, Y, Nb, Zr, Ba which are completely incompatible with olivine. The Ni 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.

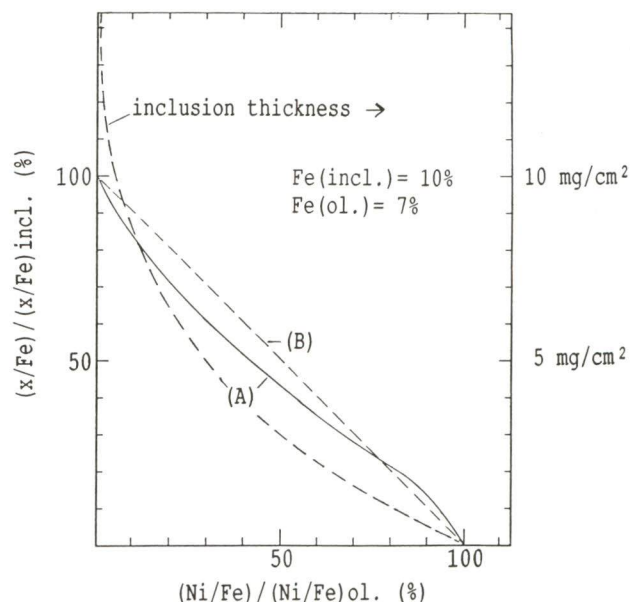


Figure 5. The Ni in the spectrum in fig. 4 is assumed to be due entirely to olivine, and thus can be used to correct the data. Theoretical calculation of the yield of elements X normalized to the Fe content as % of that from an infinitely thick sample is plotted against the corresponding ratio for Ni 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 [Hom 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 $\sim 1.6 \mu\text{m}$ [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

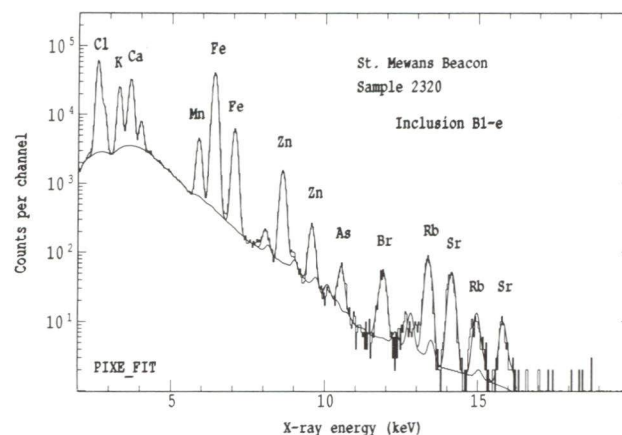


Figure 6. A typical spectrum from analysis of a fluid inclusion in quartz at about 13 μm depth below the surface. The depth is estimated from the Cl K_{α}/K_{β} ratio to an accuracy of ~ 1.6 microns [from Ryan et al, 1991].

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 cyanidization 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 [Chrysosoulis 1989, Chrysosoulis 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 [Griffin 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.

MR F 3 1 8

ANALYSIS OF CARBON CONTENT AND DISTRIBUTION IN $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ FILMS BY RESONANT SCATTERINGS.H. SIE¹⁾, D.R. McKENZIE²⁾, G.B. SMITH³⁾ and C.G. RYAN¹⁾¹⁾ CSIRO Division of Mineral Physics, PO Box 136, North Ryde, NSW, 2113, Australia²⁾ School of Physics, University of Sydney, Sydney, NSW, 2006, Australia³⁾ Department of Physics, New South Wales Institute of Technology, Sydney, NSW, 2007, Australia

Resonant alpha scattering has been used to determine detailed depth profiles of carbon in amorphous silicon carbon alloys produced by glow discharge decomposition. The carbon profiles exhibit a two layer structure similar to that indicated by hydrogen profiles in $a\text{-Si:H}$ films. By comparison electron probe analysis seems to considerably overestimate average carbon content while electron energy loss measurements on very thin specimens agree with the surface layer content in the resonance profiles of thicker films. The bulk content is, however, still lower.

1. Introduction

Amorphous hydrogenated silicon-carbon alloys have important applications in optoelectronic devices. They have a variable optical gap [1] according to the carbon content, adjustable from 1.8 eV for $a\text{-Si:H}$ through a maximum value of around 2.4 eV for intermediate compositions to 2.0 eV for $a\text{-C:H}$. The alloys can be produced by glow discharge decomposition techniques from mixtures of silane and methane. The rates of decomposition of the two gases vary with conditions of manufacture and the mixture, and thus the carbon content of the resultant material must be determined independently.

Unfortunately, although there are a number of studies of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ in the literature, most of the methods used for the analysis of film composition are dubious. It has recently been found [2] that two methods of analysis, electron probe microanalysis (EPMA) and electron energy loss spectroscopy (EELS) give results differing by as much as factor of 2. Conventional RBS (Rutherford backscattering) methods could, in favourable cases (e.g. for thick films $> 1\text{ }\mu\text{m}$), be used to determine C content, but detailed profiles cannot be determined reliably by this method. However, a strong resonance occurs at a higher bombarding energy $E_\alpha = 4.26\text{ MeV}$, which enhances the detection sensitivity and, as a result of its narrow width, enables measurements of detailed depth profiles [3].

In the following, carbon profiles in several $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ thin film samples produced by the dc magnetron glow discharge method were obtained using the resonant α scattering technique. The results are compared with other methods. The oxygen contents of some

of the samples were also examined by the resonance scattering method [4].

2. Experimental method

2.1. Sample preparation

The dc magnetron apparatus used in the production of the specimens has been described in detail elsewhere [5]. The cathode was stainless steel which was operated in a condition in which it became overcoated with silicon and carbon. Various mixtures of semiconductor grade silane (SiH_4) and ultra high purity methane (CH_4) gases were used. Operating conditions for the magnetron are shown in table 1. Substrates for the specimens were mounted on the anode. The cathode was operated for 5 min in the gases to be used for deposition before the sample was inserted. Various substrate temperatures were used, in the range 26–500°C (table 2). Film thicknesses were measured using a Talystep step height gauge.

Table 1
The deposition conditions for $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films

Discharge voltage	900 V
Current	30–50 mA
Magnetic field	0.01 T
Total gas pressure	1.2 Pa
Substrate (anode) cathode distance	30 mm
Substrate temperature	25–500°C

Table 2
Summary of samples

Sample	A	B	C	D	E	F	G	H	I
Substrate	glass	glass	Cu	glass	suprasil	Cu	glass	glass	glass
Substrate temperature (°C)	468	365	146	250	250	58	25	25	300
Methane fraction	0.50	0.50	0.50	0.50	0.25	0.5	0.67	0.50	0.50
Film thickness (Talystep) (μm)	0.97	1.3	~1	~1	0.030	1.74	~2	~1	—

2.2. Ion beam analysis

Analysis of the samples was carried out with alpha particle beams with energies in the range 2.3–4.6 MeV, supplied by a 3 MV Tandetron at the CSIRO heavy ion analytical facility (HIAF).

RBS measurements at 2.3 MeV were carried out to check the structure and the thicknesses of the films.

The carbon profiles were measured using the resonance scattering $^{12}\text{C}(\alpha, \alpha')$ at $E_\alpha = 4.26$ MeV with a width $\Gamma = 33$ keV. The characteristics of this resonance are similar to the resonance used for oxygen profiles, employing the reaction $^{16}\text{O}(\alpha, \alpha')$ at $E_\alpha = 3.036$ MeV with $\Gamma = 8.1$ keV. Both resonances show strong angular distributions peaked towards the back angles. All measurements, including RBS, were carried out with the detector angle set at 165° with respect to the beam

direction. The angular spread of the detector is 1° and the solid angle accepted was 0.9 msr.

In the case of carbon profiles, it is essential that a good vacuum is obtained before measurements commence. A base pressure of 6×10^{-8} Torr was obtained, and at this pressure there was no evidence of carbon buildup on the target under prolonged beam bombardment. The targets were stable under irradiation with beam currents as high as 100 nA, as confirmed by repeat measurements.

The total widths of the resonances including the detector resolution (18 keV) translate into 81 and 39 nm depth resolutions at the surface for C and O respectively, in pure Si. These increase to 94 and 63 nm at a depth of 1 μm in Si.

Typical spectra obtained below and just above the resonances are shown in fig. 1. Resonance yields were

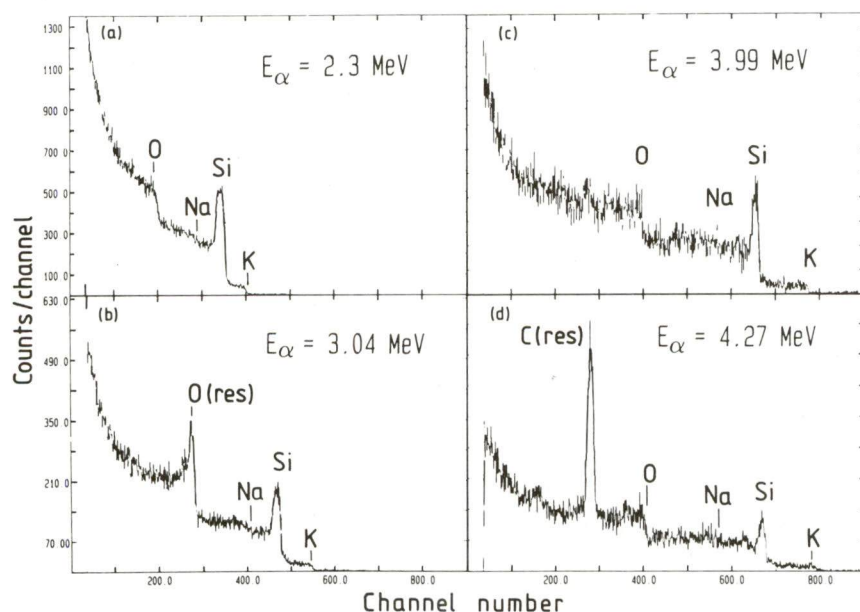


Fig. 1. An example of typical backscattered particle spectra obtained from $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ (sample H, see table 2) on glass substrates (a) below the resonances, (b) just above the oxygen resonance, (c) just below the carbon resonance and (d) just above the carbon resonance. The elements K, Na and bulk O originate from the glass substrate.

calibrated against a pure carbon (graphite) target for the carbon analysis, and against a quartz target for the oxygen analysis.

3. Results and discussion

Carbon profiles from the samples studied are shown in fig. 2. All samples exhibit a broad surface peak with widths greater than the resolution of the resonance. The possibility that these peaks are carbon buildup under beam bombardment due to residual hydrocarbons in the vacuum system is unlikely when one examines the range of intensity of these surface peaks in different samples. The presence of these peaks, which can be significantly different to the "bulk" region, point to the need for caution in the interpretation of other methods of analysis which do not give detailed depth distributions or which rely on very thin specimens. The results for the present measurements are tabulated in table 3, including EPMA results for a few of the samples. The present results are divided into the "surface region" and "bulk" components. The "surface region" was taken to be the layer corresponding to $0.25\ \mu\text{m}$ thickness (calculated assuming bulk silicon density, see fig. 2a, b) for samples A, B, E, G and to $0.5\ \mu\text{m}$ for samples C, D, F, H, I. The remainder of the thickness was defined as "bulk". The numbers obtained are necessarily coarse (with about 20% error) owing to the arbitrariness of the division. The "average" number represents an average over the thickness of the film, for the purpose of comparisons with other methods. Although these estimates involve uncertainties, especially in those cases where the profiles were not measured through the full thickness of the film, they form a useful framework for the following observations. Fig. 3 shows the observed relationship between the methane fraction of the source gas mixture and the measured carbon content by EPMA and electron energy loss (EELS) for samples produced under the same conditions, together with a selection of results from the current samples all at substrate temperatures of $250\text{--}300^\circ\text{C}$. EELS results lie above the average values, but agree well with surface region content. The EELS films, being very thin, probably only have surface characteristics. EPMA results are systematically higher

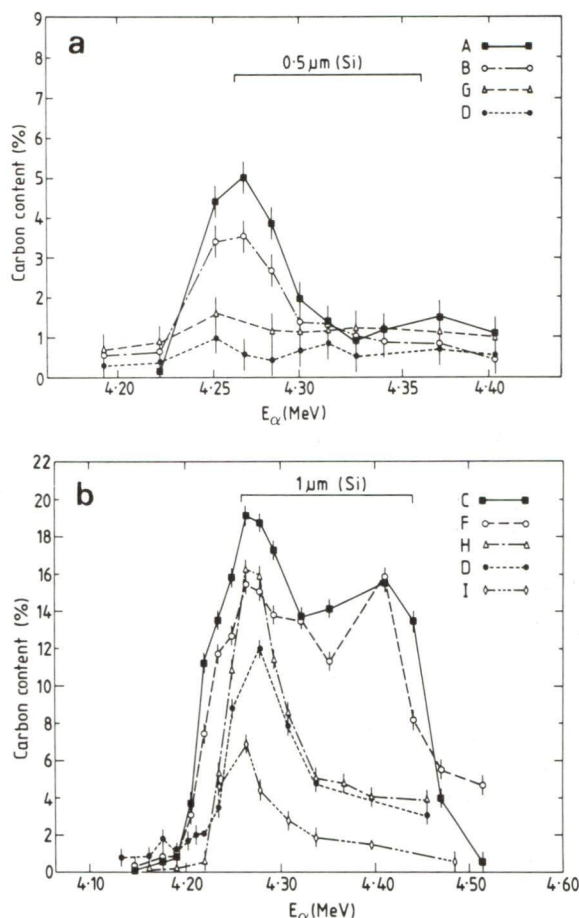


Fig. 2. Carbon profiles (in at.%) obtained from the samples tabulated in table 2. All exhibit a surface peak region at various relative intensities to the "bulk" concentrations. The depth scales indicated were calculated assuming pure silicon.

than EELS. This may reflect the uncertainty in EPMA analysis due to the very low X-ray energy ($0.282\ \text{keV}$) which can be strongly absorbed by the silicon matrix and effects of secondary fluorescence of the carbon by silicon X-rays. It is plausible that EPMA gives a correct analysis for certain depths, and when the distribution is uniform. Several works have reported good agreement between EPMA and AES analysis [1]. The latter analysed

Table 3
Carbon content of samples analyses (atomic fraction)

Sample	A	B	C	D	E	F	G	H	I
<i>This work</i>									
"Surface peak" region	0.057	0.041	0.191	0.128	0.009	0.157	0.019	0.160	0.079
"Bulk"	0.014	0.011	0.152	0.049	0.007	0.138	0.016	0.047	0.017
Average	0.035	0.030	0.172	0.089	0.008	0.148	0.0175	0.103	0.048
EPMA	0.20	0.25	0.20						

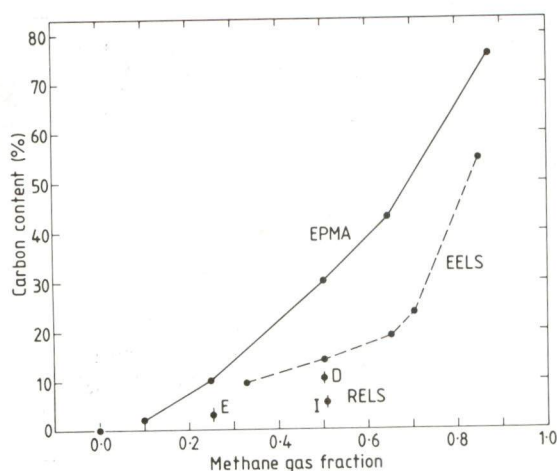


Fig. 3. Results of various methods of analysis for carbon content (in at.%) as a function of the methane gas fraction in the source gas for samples produced at 250–300°C substrate temperature. EPMA – electron probe micro analysis, EELS – electron energy loss analysis, RELS – resonant elastic scattering (samples D, E, I).

samples to depths up to around 20 Å, thus sampling only the surface layer.

When a strong variation in C concentration occurs in samples such as those studied here, particularly in samples with lower C content, EPMA will give erroneous average concentrations when compared to resonant scattering measurements covering the whole thickness of the sample. All profiles measured here show strong surface peaks extending to depths of $\sim 0.3 \mu\text{m}$. EPMA analysis sampling the surface peak would thus be likely to result in an overestimate of the average concentration. EELS indicates that very thin films, prepared

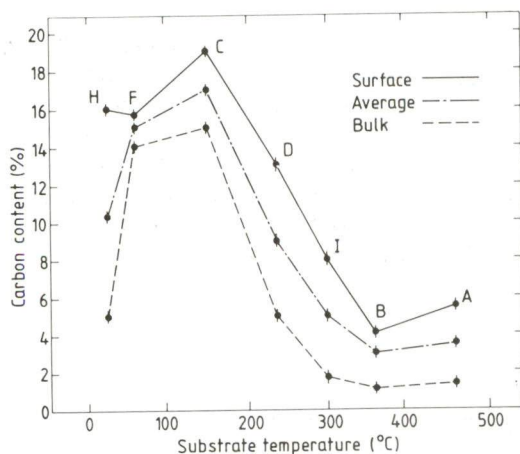


Fig. 4. Substrate temperature dependence of the carbon content (in at.%) for a 50% silane/50% methane gas mixture. The values shown are averaged over the thickness of the films. The samples are all relatively rich in Si, especially at higher substrate temperature.

under the same conditions as our thicker films, appear not to develop bulk characteristics.

The carbon profiles in the present samples indicate the existence of a two layer structure, such as that deduced from hydrogen profiles in amorphous hydrogenated silicon films produced by glow discharge decomposition [6]. In the present case the carbon profile is the indicator of this structure, as H was in the case of a-Si:H films. Hydrogen profile measurements are in progress currently to check if there is correlation between C and H profiles. The oxygen profiles measured in a few of the samples do not show any correlation with the carbon profiles. All cases studied indicate very low concentrations of oxygen, which appear mainly near the film–substrate interface. Some of this oxygen may be due to mixing effects from the substrate.

The average concentrations produced with a 50% silane/50% methane mixture are shown in fig. 4. Despite the large range of concentration in each sample due to the presence of “surface” layers, they are rich in silicon. Of most significance is the strong dependence on the substrate temperature. Higher temperatures result in even more silicon rich films, with a transition in the region of 200–300°C (fig. 4).

The higher temperatures also appear to result in samples with strong surface peaks, with the sample produced at 146°C showing the broadest peak.

4. Conclusions

The resonance scattering technique proved to be a useful method for determining depth profiles of carbon, and also of oxygen, in thin films of $\text{a-Si}_{1-x}\text{C}_x\text{:H}$. The typically detailed structure of the profiles, with varying surface region to bulk ratios of concentration, may partially explain the large discrepancy between this method and electron probe methods, which only sample the surface region, but other sources of error are apparent in EPMA. Electron energy loss spectroscopy of very thin films produced under the same conditions gives concentrations in agreement with surface layer content but above bulk values. Bulk characteristics have thus not developed in the EELS samples.

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MR F 3 1 7

DEPTH PROFILES OF HYDROGEN AND OXYGEN IN HYDROGENATED AMORPHOUS SILICON THIN FILMS

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Detailed depth profiles of hydrogen and oxygen have been measured in samples of thin films of a-Si:H produced by dc magnetron glow discharge techniques. The resonant capture reaction $^1\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}$ at $E_{^{19}\text{F}} = 6.417$ MeV was used for hydrogen profile measurements, and resonant α scattering at $E_\alpha = 3.0359$ MeV was used for oxygen. Contrasting results reflecting the different fabrication conditions were obtained and these were correlated with measured electrical properties.

1. Introduction

The electrical and optical properties of a-Si:H produced by glow discharge decomposition of silane are related to the distribution of hydrogen. Incorporated in the silicon network, hydrogen increases dopability by terminating dangling bonds [1]. However hydrogen may also be present in other forms, particularly as hydroxyls when moisture absorption occurs, which could be detrimental to the electrical properties.

The presence of oxygen in the bulk of a semiconductor can also affect its electrical properties, and on the surface it can affect contact properties, which are important for device applications. Surface defects may in fact dominate electrical properties by creating mobile carrier accumulation layers [2]. Oxidation can be expected to be one source of oxygen, but a major contribution could come from adsorption and absorption of moisture into microvoids, typically found in films of semiconductor produced by vacuum deposition techniques. The porosity of the films depends on the fabrication conditions, and thus the hydrogen and oxygen contents may be used to diagnose the effects of different conditions.

In the following, a number of samples of thin films of a-Si:H produced by dc magnetron glow discharge have been studied. Hydrogen profiles were determined using the $^1\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}$ resonant reaction at a ^{19}F bombarding energy of 6.417 MeV. Preliminary results of these measurements have been reported [3].

Oxygen content is usually determined as part of the hydroxyl using the infrared absorption (IR) technique [4], which does not provide depth profile information. Some attempts have been made to measure oxygen profiles using Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS), but quantita-

tive interpretation of the resultant data is difficult [5]. Electron energy loss spectroscopy (EELS) and Rutherford back scattering spectrometry (RBS) can yield information on depth profiles, but the nuclear reactions $^{18}\text{O}(p, \alpha)^{15}\text{N}$ and $^{18}\text{O}(p, \gamma)^{19}\text{F}$ are more commonly used [6]. These reactions however rely on the rare isotope ^{18}O , and are therefore impractical due to the reduced sensitivity in natural targets. The deuteron reactions $^{16}\text{O}(d, p)$ or (d, n) have also been used, but the high radiation background produced by these beams makes the technique less attractive [6].

In this paper, we report the use of resonant α scattering to determine the oxygen profiles, exploiting the resonance at an α bombarding energy of $E_\alpha = 3.0359$ MeV. Results are presented together with hydrogen profiles obtained from the same specimens, to delineate the sources of these elements and correlate them with the properties of the samples.

2. Experimental procedure

2.1. Film preparation

Various parameters in the glow discharge deposition of a-Si:H in the dc magnetron system have a considerable impact on the electrical, optical and mechanical properties of the films [7]. In particular, very significant differences are observed between samples prepared with the substrate at cathode potential, where there is considerable bombardment by energetic positive ions and also fast deposition rates of up to 3.5 nm/s. Electrical measurements have indicated that the surfaces play a more significant role under these conditions, and one aim of this study was to see whether the hydrogen and oxygen profiles could be used to distinguish between

Table 1
Preparation conditions for a-Si:H samples

Sample	Electrode	Power dissipated (W)	Silane pressure (mbar)	Deposition rate (nm/s)	Magnetic field (T)	Substrate temperature (°C)
A	anode	25	0.0076	0.10	0.05	315
B	anode	57	0.0078	0.58	0.05	370
C	cathode	23	0.040	2.67	0.03	320

those surface effects due to the production process and those due to subsequent adsorption.

Other parameters of importance are substrate temperature, SiH_4 partial pressure, power dissipated in the discharge, and strength of the magnetron field. For anodic deposition higher deposition rates produce better electrical properties [7]. Full details of the deposition system are given elsewhere [7,8].

Table 1 summarizes the central parameters for the three films analysed in this study. Two are anodic, and differ only in deposition rate, the other is cathodic. Microscope glass slides were used as substrates. For IR measurements of samples A and B, a thin Al layer (~ 50 nm) was evaporated onto the substrate prior to the a-Si deposition.

2.2. Film properties

Thickness was measured with a step profiling stylus (Talystep). The thickness of the samples on the same substrate varies (by $\sim 20\%$) monotonically across the length of the substrate as a result of the configuration of the apparatus. Dark conductivity (σ_d) and photoconductivity (σ_{ph}) were measured in a gap cell geometry. Of particular significance to this work is the magnitude of dark conductivity with $\sigma_d < 10^{-9} (\Omega \text{ cm})^{-1}$ denoting minimal surface effects and $\sigma_d > 10^{-5} (\Omega \text{ cm})^{-1}$ denoting a dominance of surface effects. This in turn influences the photoconductivity for reasons discussed by Smith and McKenzie [9], such that the essential parameter for evaluating the effect of surface layers is the gain in conductivity on illumination as a ratio rather than a magnitude, that is σ_{ph}/σ_d . These parameters are all summarized in table 2. Clearly the ratio of σ_{ph}/σ_d rises as σ_d falls and the cathodic sample appears to be influenced much more than the other two by surface effects.

2.3. Ion beam analysis

The hydrogen and oxygen profiles as well as RBS measurements were performed at the CSIRO Heavy Ion Analytical Facility (HIAF), an accelerator laboratory based on a 3 MV Tandatron.

The resonant capture reaction $\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}$ at a

fluorine bombarding energy of 6.417 MeV was used in the hydrogen profile measurements. This resonance, while not as strong as the more commonly used one at $E_{^{19}\text{F}} = 16.44$ MeV, gives better depth resolution and is more isolated giving a larger accessible depth range. Using the definition of depth resolution given, for example, in ref. [10], the resonance width of 45 keV translates into a 11 nm depth resolution in pure silicon at the surface, increasing to 27 nm at $1 \mu\text{m}$ depth.

The unique reaction γ rays of 6.1 MeV were detected in a pair of 7.5 cm diameter $\times$ 20 cm long NaI detectors placed outside the vacuum chamber 3 cm from the target. The close geometry helped to minimize the relative cosmic ray background. Resonance yields between 3.5 and 7.0 MeV were measured relative to polyethylene ($(\text{CH}_2)_n$) and mylar ($\text{C}_{10}\text{H}_8\text{O}_4$) targets. Normalized to their respective hydrogen contents, these two targets gave similar results (within 2%). Measurements on these targets were carried out with less than 2 nA beam currents, and the decreasing yield due to target decomposition was monitored as a function of irradiation dose. The maximum yield, corresponding to the initial condition, was obtained by extrapolation to zero irradiation time. The actual samples studied appeared to be stable under bombardment with beam currents as high as 100 nA.

All measurements were carried out in a vacuum of $\leq 1 \times 10^{-7}$ mbar and no trace of carbon build up on the target was observed.

RBS was used primarily to check the areal density of the samples employing beams of 2.3 MeV α particles. The backscattered particles were measured with a surface barrier detector at 165° with respect to the beam direc-

Table 2
Film properties

Sample	Dark conductivity at 300 K $\sigma_d (\Omega \text{ cm})^{-1}$	Photo-conductivity at 300 K $\sigma_{ph} (\Omega \text{ cm})^{-1}$	$\frac{\sigma_{ph}}{\sigma_d}$
A	$\sim 10^{-7}$	$\sim 5 \times 10^{-5}$	500
B	6.4×10^{-10}	1.9×10^{-6}	3000
C	1.2×10^{-4}	5×10^{-4}	4

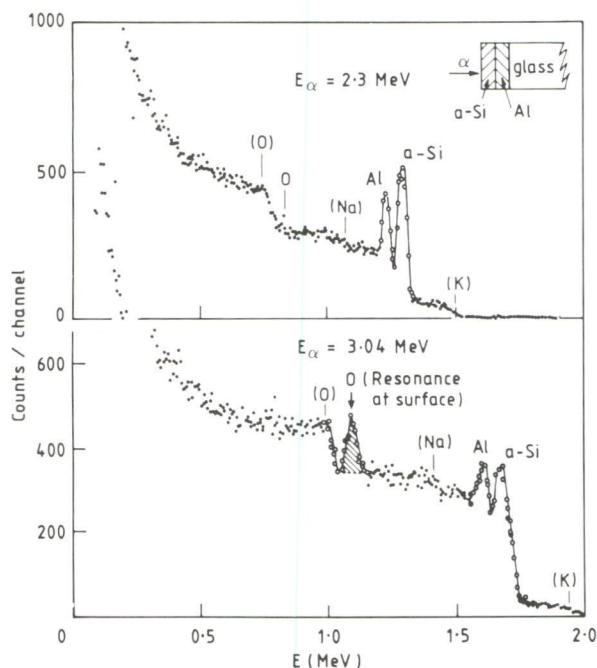


Fig. 1. Typical spectra from an a-Si:H sample taken below and above the resonance at $E_{\alpha} = 3.0359$ MeV. This sample (A) was produced on a glass substrate coated first with a thin Al layer. The thick target features of elements K, Na, O originate from the glass substrate.

tion, at a distance of 75 mm, subtending a solid angle of 0.9 msr at the target.

The same experimental setup was used for the oxygen profile measurements, employing the resonant α scattering at an incident beam energy of 3.0359 MeV. Although this resonance has been known for some time [11], it has only recently been used in profiling [12]. The angular distribution at the resonance is peaked towards the back angles, and consequently measurements were carried out at the furthest angle in the backward direction of 165° . The resonance yield was measured relative to a fused quartz target, which is assumed to be pure SiO_2 , confirmed by RBS. The RBS and resonant scattering spectra are shown in fig. 1. The width of the resonance (8.1 keV) is less than the detector resolution of 18 keV. Using the same definition [10], the depth resolution from the total width is 39 nm, increasing to 63 nm at $1 \mu\text{m}$ depth in pure silicon.

3. Results and discussion

Hydrogen profiles from the three samples are shown in fig. 2. Results from samples A and B have been reported previously [3]. The substrate interface can be discerned as a rapid drop in H content in samples A

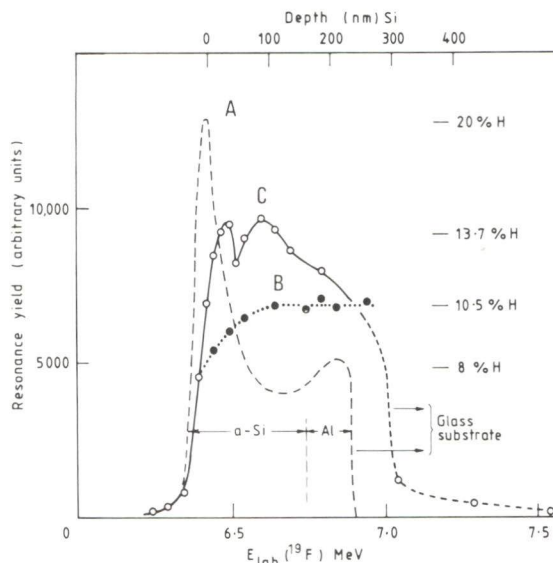


Fig. 2. Hydrogen profiles in the three a-Si:H samples studied. Conditions of manufacture of the samples are given in table 1. A depth scale to guide the reader is calculated for pure silicon.

and C. For sample B, the substrate interface was not reached in these measurements. The cathodic deposition (sample C) results in a higher bulk hydrogen content, with some structure near the surface. Results for the oxygen profiles are shown in fig. 3. For samples A and C the substrate interface can be discerned as the part with a similar profile to quartz. Again for sample B the measurements did not extend to the substrate. The high O content in sample A made it possible to separate the resonance yield from the sample and that of the substrate. The glass substrates used provided a convenient check on the resonance yield calibration, as well as on the thickness of the film. This can be obtained from the shift of the resonance curve from the glass backing which has a similar shape to that obtained from quartz. For samples A and B, the film thicknesses can also be deduced from the hydrogen profiles, but due to the variation in thickness the results do not necessarily agree exactly with those obtained from the resonant RBS measurements. Because three components are involved, the relations between the atomic concentrations of H and O and their respective resonance yields are not linear. The values shown in the figures corresponding to major features of the profiles were obtained by iteration.

The need for both hydrogen and oxygen profiles is apparent when the profiles and electrical data are interpreted together.

The greatest surprise was the oxygen profile in the ion bombarded sample C. This profile indicates no oxygen related surface structure (fig. 3), contrary to

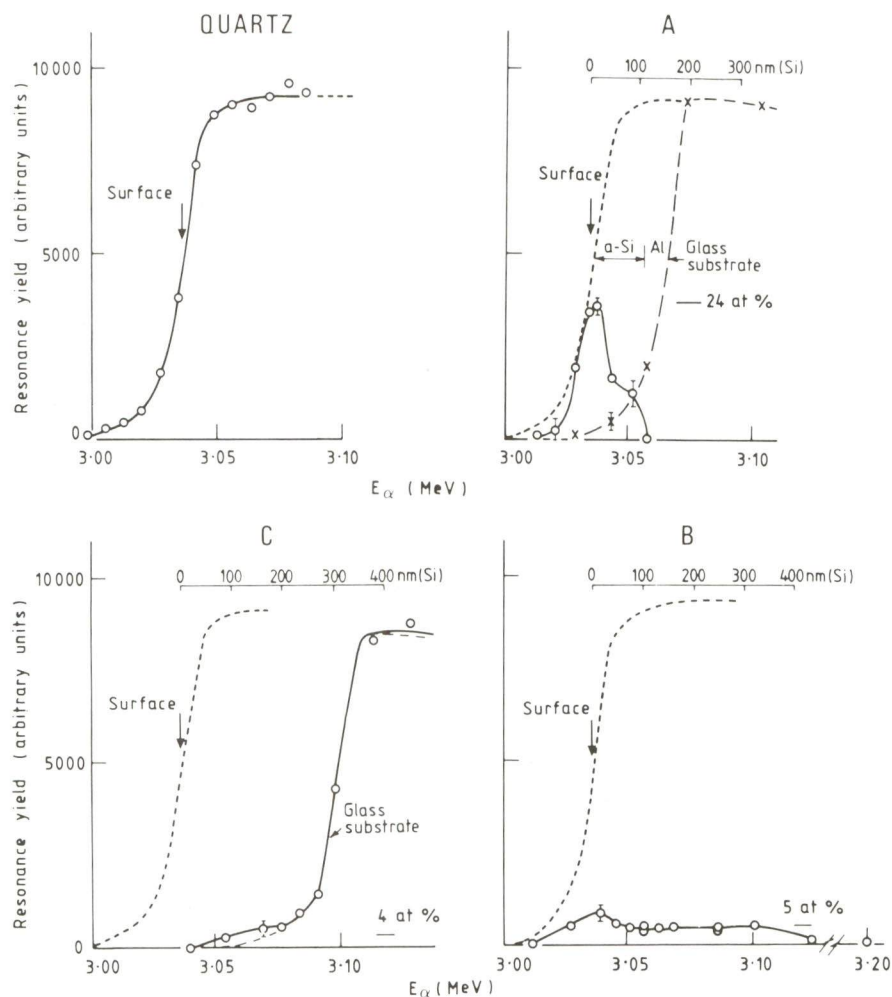


Fig. 3. Oxygen profiles corresponding to the resonance yield measured on fused quartz and the a-Si:H samples. Depth scales, again only to be used as a guide, are given for pure silicon. The glass substrate can be identified as the part resembling the quartz profile.

expectations based on the electrical properties. However, a definite surface layer ~ 40 nm thick is seen in the hydrogen profile. The surface profiles of H have been referred to by others [13] with the significant drop in concentration indicative of a boundary between a surface layer of different structure to the bulk. The evidence is mainly obtained from nuclear reaction studies but other techniques such as permeability [13] have produced similar evidence.

The excess hydrogen relative to oxygen observed for the surface region in samples B and C (fig. 2) cannot be accounted for in terms of moisture adsorption only. The possibility that hydrocarbons may be adsorbed on the surface [13] is unlikely in the present case. In the production of the samples, the hydrocarbon partial pressure due to possible backstreaming of contaminants from the vacuum pumps at a base pressure of 10^{-7} mbar would be negligible compared to the source gas

(silane) pressure. In the ion-beam analyses, no evidence of carbon build up on the samples under beam bombardment was observed, indicating minimal or no hydrocarbon contamination. Possible contribution from the vacuum system is further eliminated when the same profiles were obtained from repeat measurements.

It is more likely the hydrogen rich surface is an intrinsic property of the surface. Growth models have been postulated which provide a surface layer ~ 20 nm thick with different properties to the bulk [13]. This hydrogen rich layer may represent an incomplete reaction zone with an excess of dangling bonds with molecular hydrogen or other forms containing hydrogen in the microvoids. Such a zone could be expected to extend deeper in ion bombarded samples, as in sample C, due to mixing effects between layers during growth.

The cathodic films are also extremely adherent as deduced from a scratch test. The rise in the oxygen

profile near the substrate where the hydrogen falls off indicates ion mixing with the substrate, which could provide greater mechanical strength. By contrast with sample A (see below), the film is not very porous so that there is little scope for adsorption.

The two anodic samples are quite different to the cathodic sample and to each other. Here the evidence for a surface layer which might influence electrical behaviour, as observed, is clear cut for A. The atomic ratios of hydrogen (~ 20 at.%) and oxygen (~ 24 at.%) indicate other sources of oxygen, such as surface oxide. But the main source, given the close correlation of the oxygen and hydrogen profiles over the full film, is either adsorbed water or hydroxyl. The thickness of surface peaks in both the H and O profiles for this sample A appears to be ~ 100 nm, showing a significant level of penetration of water or hydroxyl into the film bulk. This in turn denotes high porosity, particularly in the surface region.

Sample B, in contrast to both other samples, shows a surface depleted in hydrogen and no clear cut demarcation zone but a gradual rise to the bulk value. A weak surface oxide peak is however observed. Electrically this film is the best of those analysed here (low dark current and high σ_{ph}/σ_d), although significantly better results have been produced using this technique [9]. This film is very much softer (as shown by the scratch test) than sample C and is less dense, as deduced from IR reflectivity. The porosity or void structure in these anodic films appears to be strongly influenced by deposition rate.

In sample B the correlation of hydrogen and oxygen is relatively constant in the vicinity of the surface. This indicates the probable penetration of water into the film. However the depth at which the oxygen become negligible is well away from the film-substrate interface. This film has much less water penetration than its more slowly deposited counterpart, sample A. The reduced hydrogen at the surface of B could be due in part to the higher substrate temperature.

4. Conclusions

Films produced anodically by the dc magnetron glow discharge system were shown previously [7] to have improved electrical properties at higher deposition rates; the increased rate also improved the quality of solar cells [14]. This improvement can be associated with a decrease in porosity deduced from a lower moisture intake, as implied from the oxygen and hydrogen profiles.

Similar deductions for the cathodic samples imply that they have low porosity, however their electrical properties are dominated by surface layer effects. Results of the present study suggest that these surface effects are linked to a distinct surface layer which is hydrogen rich as a result of the growth process under these conditions of strong ion bombardment.

References

- [1] J.D. Joannopoulos and G. Lucovsky (eds.), *Physics of Hydrogenated Amorphous Silicon*, vol. 1 (Springer Verlag, Berlin, 1984).
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- [3] S.H. Sie, D.R. McKenzie and G.B. Smith, *Appl. Surf. Sci.* 22/23 (1985) 916.
- [4] M.H. Brodsky, M. Cardona and J.C. Knights, *Phys. Rev.* B16 (1977) 3556.
- [5] W. Reuter, *Nucl. Instr. and Meth.* 218 (1983) 391.
- [6] J.F. Ziegler (ed.), *New Uses of Ion Accelerators* (Plenum Press, New York, 1975).
- [7] G.B. Smith and D.R. McKenzie, *Solar Energy Mater.* 11 (1984) 45.
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- [10] C.A. Barnes, J.C. Overley, Z.E. Switkowski and T.A. Tombrello, *Appl. Phys. Lett.* 31 (1977) 239.
- [11] J.R. Cameron, *Phys. Rev.* 90 (1953) 839.
- [12] S. Petersson, H. Norde, G. Possnert and B. Orre, *Nucl. Instr. and Meth.* 149 (1978) 285.
- [13] E. Sacher, J. Klemberg-Sapieha, M.R. Wertheimer, H.P. Schreiber and R. Groleau, *Philos. Mag.* B49 (1984) L47.
- [14] G.B. Smith and D.R. McKenzie, *Appl. Surf. Sci.* 22/23 (1985) 891.

Withdrawal/Redaction Sheet

(George Bush Library)

Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
01d. Letter	To: Soey Hian Sie From: Allan Bromley Re: response to request for recommendation [personal information redacted] (1 pp.)	12/18/92	(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
Re-review Case #:		Appeal Disposition:	
P-2/P-5 Review Case #:		Disposition Date:	
AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

RESTRICTION CODES

Presidential Records Act - [44 U.S.C. 2204(a)]

P-1 National Security Classified Information [(a)(1) of the PRA]
 P-2 Relating to the appointment to Federal office [(a)(2) of the PRA]
 P-3 Release would violate a Federal statute [(a)(3) of the PRA]
 P-4 Release would disclose trade secrets or confidential commercial or
 financial information [(a)(4) of the PRA]
 P-5 Release would disclose confidential advice between the President
 and his advisors, or between such advisors [(a)(5) of the PRA]
 P-6 Release would constitute a clearly unwarranted invasion of
 personal privacy [(a)(6) of the PRA]

C. Closed in accordance with restrictions contained in donor's deed of gift.

PRM. Removed as a personal record misfile.

Freedom of Information Act - [5 U.S.C. 552(b)]

(b)(1) National security classified information [(b)(1) of the FOIA]
 (b)(2) Release would disclose internal personnel rules and practices of an
 agency [(b)(2) of the FOIA]
 (b)(3) Release would violate a Federal statute [(b)(3) of the FOIA]
 (b)(4) Release would disclose trade secrets or confidential or financial
 information [(b)(4) of the FOIA]
 (b)(6) Release would constitute a clearly unwarranted invasion of
 personal privacy [(b)(6) of the FOIA]
 (b)(7) Release would disclose information compiled for law enforcement
 purposes [(b)(7) of the FOIA]
 (b)(8) Release would disclose information concerning the regulation of
 financial institutions [(b)(8) of the FOIA]
 (b)(9) Release would disclose geological or geophysical information

TYPE: ACTION
ORIGINATOR: 02

STATUS I

DOCUMENT NUMBER: 9203622
DIRECTORATE STATUS

FROM: JOHNSTON, Timothy A.

TO: DR. D.A. BROMLEY

DATE OF
CORRESPONDENCE: 12/03/92

SUBJECT: HE IS WRITING FOR A REFERENCE FOR GRADUATE SCHOOL.

DIRECTORATE STAFF
ASSIGNED: D. Allan Bromley ASSIGNED:

ACTION STAFF
REQUIRED: DIRECT REPLY ACTION:

SENDER'S DUE DATE: 01/18/92
OSTP DUE DATE: 01/11/92 STAFF DUE DATE
DATE COMPLETED: DATE COMPLETED/DEPT:

COPIES TO:

WHITE HOUSE TRACKING #: CONTACT PERSON:
REMARKS: PHONE: EXT:

OSTP RECEIVED: 12/18/92 DEPT RECEIVED:
FILE: P-DAB-REFERRAL

CENTRAL FILES:

Withdrawal/Redaction Sheet

(George Bush Library)

Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
02a. Letter	To: Allan Bromley From: Timothy Johnston Re: Request for letter of recommendation [personal information redacted] (1 pp.)	12/3/92	(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
Re-review Case #:		Appeal Disposition:	
P-2/P-5 Review Case #:		Disposition Date:	
AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

RESTRICTION CODES

Presidential Records Act - [44 U.S.C. 2204(a)]

P-1 National Security Classified Information [(a)(1) of the PRA]
P-2 Relating to the appointment to Federal office [(a)(2) of the PRA]
P-3 Release would violate a Federal statute [(a)(3) of the PRA]
P-4 Release would disclose trade secrets or confidential commercial or
financial information [(a)(4) of the PRA]
P-5 Release would disclose confidential advice between the President
and his advisors, or between such advisors [(a)(5) of the PRA]
P-6 Release would constitute a clearly unwarranted invasion of
personal privacy [(a)(6) of the PRA]

C. Closed in accordance with restrictions contained in donor's deed of
gift.

PRM. Removed as a personal record misfile.

Freedom of Information Act - [5 U.S.C. 552(b)]

(b)(1) National security classified information [(b)(1) of the FOIA]
(b)(2) Release would disclose internal personnel rules and practices of an
agency [(b)(2) of the FOIA]
(b)(3) Release would violate a Federal statute [(b)(3) of the FOIA]
(b)(4) Release would disclose trade secrets or confidential or financial
information [(b)(4) of the FOIA]
(b)(6) Release would constitute a clearly unwarranted invasion of
personal privacy [(b)(6) of the FOIA]
(b)(7) Release would disclose information compiled for law enforcement
purposes [(b)(7) of the FOIA]
(b)(8) Release would disclose information concerning the regulation of
financial institutions [(b)(8) of the FOIA]
(b)(9) Release would disclose geological or geophysical information

NATIONAL SCIENCE FOUNDATION
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**Reference Report
On Applicant**Administered by the National Research Council
Fellowship Office, 2101 Constitution Avenue, Washington, D.C. 20418
Awardees Selected by the National Science Foundation.

Please type.

Name of

Respondent

Title

Respondent's

Department

Respondent's

Institution

To be completed by applicant:

Name of Applicant

.....Johnston.....Timothy.....Armstrong.....
last first middle maiden

FieldDevelopment Studies.....

(e.g., Microbiology, Theoretical Physics)

Date DueJanuary 18, 1993.....

(See Application Instructions)

ACQUAINTANCE WITH APPLICANT:

1. I have known the applicant for a period of years and/or months.
2. I have known the applicant as ☐ an undergraduate ☐ a research assistant ☐ other(specify).....
☐ a graduate student ☐ a teaching assistant
3. I have served as the applicant's ☐ research adviser ☐ teacher in several classes ☐ department chair
☐ major adviser ☐ teacher in only one class ☐ other (specify).....

4. **APPLICANT'S SCHOLARLY CHARACTERISTICS:** Please rate the applicant in comparison with other students whom you have known in similar stages of their academic careers:

	Truly Exceptional (Top 1%)	Outstanding (Top 5%)	Excellent (Top 10%)	Very Good (Top 25%)	Satisfactory (Top 50%)	Below Average (Lower 50%)	No Basis for Judgment
Knowledge in chosen field							
Motivation and perseverance toward educational goals							
Ability to work independently							
Ability to work as a member of a research team							
Ability to plan and conduct research							
Ability in: Oral expression							
Written expression							
Imagination and probable creativity							

5. **APPLICANT'S OVERALL SCIENTIFIC ABILITY:** Please indicate the strength of your overall endorsement of this applicant for an NSF Graduate Research Fellowship by placing a single checkmark in one of the boxes:

1	2	3	4	5	6	No Basis for Judgment
Truly Exceptional (Top 1%)	Outstanding (Top 5%)	Excellent (Top 10%)	Very Good (Top 25%)	Satisfactory (Top 50%)	Below Average (Lower 50%)	

Please turn to the other side of the form to complete this reference.

IMPORTANT — CONFIDENTIALITY: Before signing this report, you should check one of the two blocks at the right as applicable. If block A is checked, the Foundation will hold your comments in confidence so as not to reveal your identity as the author of these comments, but warns that failure to check block A may result in a requirement to provide these comments to the applicant under the Privacy Act of 1974.

☐ A. My preparation of this Reference Report is conditioned on the promise of the Foundation to hold my identity as the author of these comments in confidence.

☐ B. My preparation of this Reference Report is *not* conditioned on the promise of the Foundation to hold my comments in confidence.

Signature of Respondent: Date:

To the Respondent: When you have completed and signed this reference, please return it to the applicant in the envelope provided.

Withdrawal/Redaction Sheet

(George Bush Library)

Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
02b. Resume	Resume of Timothy A. Johnston [personal information redacted] (2 pp.)	12/3/92	(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
Re-review Case #:		Appeal Disposition:	
P-2/P-5 Review Case #:		Disposition Date:	
AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

RESTRICTION CODES

Presidential Records Act - [44 U.S.C. 2204(a)]

P-1 National Security Classified Information [(a)(1) of the PRA]
P-2 Relating to the appointment to Federal office [(a)(2) of the PRA]
P-3 Release would violate a Federal statute [(a)(3) of the PRA]
P-4 Release would disclose trade secrets or confidential commercial or financial information [(a)(4) of the PRA]
P-5 Release would disclose confidential advice between the President and his advisors, or between such advisors [(a)(5) of the PRA]
P-6 Release would constitute a clearly unwarranted invasion of personal privacy [(a)(6) of the PRA]

C. Closed in accordance with restrictions contained in donor's deed of gift.

PRM. Removed as a personal record misfile.

Freedom of Information Act - [5 U.S.C. 552(b)]

(b)(1) National security classified information [(b)(1) of the FOIA]
(b)(2) Release would disclose internal personnel rules and practices of an agency [(b)(2) of the FOIA]
(b)(3) Release would violate a Federal statute [(b)(3) of the FOIA]
(b)(4) Release would disclose trade secrets or confidential or financial information [(b)(4) of the FOIA]
(b)(6) Release would constitute a clearly unwarranted invasion of personal privacy [(b)(6) of the FOIA]
(b)(7) Release would disclose information compiled for law enforcement purposes [(b)(7) of the FOIA]
(b)(8) Release would disclose information concerning the regulation of financial institutions [(b)(8) of the FOIA]
(b)(9) Release would disclose geological or geophysical information

"Document Control"

TYPE: ACTION DOCUMENT NUMBER: 9203541
ORIGINATOR: 02 STATUS I DIRECTORATE STATUS

FROM: SALE, Stephen: FEHRENBACHER, SALE, QUINN & DEESE

TO: DR. D.A. BROMLEY

DATE OF
CORRESPONDENCE: 12/01/92

SUBJECT: HE IS ASKING DR. BROMLEY TO WRITE A LETTER ON BEHALF
OF DR. ZAHID AND HIS EFFORTS TO SECURE A VISA FOR
HIS WIFE.

DIRECTORATE STAFF
ASSIGNED: D. Allan Bromley ASSIGNED:

ACTION STAFF
REQUIRED: AS APPROPRIATE ACTION:

SENDER'S DUE DATE:
OSTP DUE DATE: 12/18/92 STAFF DUE DATE
DATE COMPLETED: DATE COMPLETED/DEPT:

COPIES TO:

WHITE HOUSE TRACKING #: CONTACT PERSON:
REMARKS: PHONE: EXT:

OSTP RECEIVED: 12/07/92
FILE: P-DAB-PERSONAL

DEPT RECEIVED:

CENTRAL FILES:

Withdrawal/Redaction Sheet

(George Bush Library)

Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
03a. Letter	To: Allan Bromley From: Stephen Sale Re: Request for letter of behalf of Dr. Zahid and his wife [personal information redacted] (2 pp.)	12/1/92	(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
Re-review Case #:		Appeal Disposition:	
P-2/P-5 Review Case #:		Disposition Date:	
AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

RESTRICTION CODES

Presidential Records Act - [44 U.S.C. 2204(a)]

P-1 National Security Classified Information [(a)(1) of the PRA]
P-2 Relating to the appointment to Federal office [(a)(2) of the PRA]
P-3 Release would violate a Federal statute [(a)(3) of the PRA]
P-4 Release would disclose trade secrets or confidential commercial or financial information [(a)(4) of the PRA]
P-5 Release would disclose confidential advice between the President and his advisors, or between such advisors [(a)(5) of the PRA]
P-6 Release would constitute a clearly unwarranted invasion of personal privacy [(a)(6) of the PRA]

C. Closed in accordance with restrictions contained in donor's deed of gift.

PRM. Removed as a personal record misfile.

Freedom of Information Act - [5 U.S.C. 552(b)]

(b)(1) National security classified information [(b)(1) of the FOIA]
(b)(2) Release would disclose internal personnel rules and practices of an agency [(b)(2) of the FOIA]
(b)(3) Release would violate a Federal statute [(b)(3) of the FOIA]
(b)(4) Release would disclose trade secrets or confidential or financial information [(b)(4) of the FOIA]
(b)(6) Release would constitute a clearly unwarranted invasion of personal privacy [(b)(6) of the FOIA]
(b)(7) Release would disclose information compiled for law enforcement purposes [(b)(7) of the FOIA]
(b)(8) Release would disclose information concerning the regulation of financial institutions [(b)(8) of the FOIA]
(b)(9) Release would disclose geological or geophysical information

Withdrawal/Redaction Sheet

(George Bush Library)

Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
03b. Letter	To: Mary Ann Carey, Ambassador to Algeria, From: Allan Bromley Re: Support for visa application for Dr. Zahid and his wife [personal information redacted] (1 pp.)		(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
Re-review Case #:		Appeal Disposition:	
P-2/P-5 Review Case #:		Disposition Date:	
AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

RESTRICTION CODES

Presidential Records Act - [44 U.S.C. 2204(a)]

P-1 National Security Classified Information [(a)(1) of the PRA]
P-2 Relating to the appointment to Federal office [(a)(2) of the PRA]
P-3 Release would violate a Federal statute [(a)(3) of the PRA]
P-4 Release would disclose trade secrets or confidential commercial or financial information [(a)(4) of the PRA]
P-5 Release would disclose confidential advice between the President and his advisors, or between such advisors [(a)(5) of the PRA]
P-6 Release would constitute a clearly unwarranted invasion of personal privacy [(a)(6) of the PRA]

C. Closed in accordance with restrictions contained in donor's deed of gift.

PRM. Removed as a personal record misfile.

Freedom of Information Act - [5 U.S.C. 552(b)]

(b)(1) National security classified information [(b)(1) of the FOIA]
(b)(2) Release would disclose internal personnel rules and practices of an agency [(b)(2) of the FOIA]
(b)(3) Release would violate a Federal statute [(b)(3) of the FOIA]
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(b)(8) Release would disclose information concerning the regulation of financial institutions [(b)(8) of the FOIA]
(b)(9) Release would disclose geological or geophysical information

"Document Control"

TYPE: ACTION DOCUMENT NUMBER: 9203509
ORIGINATOR: 02 STATUS I DIRECTORATE STATUS

FROM: ROSENFELD, LOUIS: NYU MEDICAL CENTER

TO: DR. D.A. BROMLEY

DATE OF
CORRESPONDENCE: 11/23/92

SUBJECT: REQUEST TO SEND A LETTER OF SUPPORT TO HONOR BOTH
OTTO FOLIN AND DONALD VAN SLYKE ON A U.S. POSTAGE
STAMP.

DIRECTORATE STAFF
ASSIGNED: D. Allan Bromley ASSIGNED:

ACTION STAFF
REQUIRED: AS NECESSARY ACTION:

SENDER'S DUE DATE:
OSTP DUE DATE: 12/09/92 STAFF DUE DATE
DATE COMPLETED: DATE COMPLETED/DEPT:

COPIES TO:

WHITE HOUSE TRACKING #: CONTACT PERSON:
REMARKS: PHONE: EXT:

OSTP RECEIVED: 12/02/92 DEPT RECEIVED:
FILE: P-DAB-REFERRAL
CENTRAL FILES:

Withdrawal/Redaction Sheet

(George Bush Library)

Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
04a. Letter	To: Allan Bromley From: Louis Rosenfeld Re: Requests Letter of Recommendation for Otto Folin and Donald Van Slyke [personal information redacted] (1 pp.)	11/23/92	(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
Re-review Case #:		Appeal Disposition:	
P-2/P-5 Review Case #:		Disposition Date:	
AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

RESTRICTION CODES

Presidential Records Act - [44 U.S.C. 2204(a)]

P-1 National Security Classified Information [(a)(1) of the PRA]
P-2 Relating to the appointment to Federal office [(a)(2) of the PRA]
P-3 Release would violate a Federal statute [(a)(3) of the PRA]
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P-5 Release would disclose confidential advice between the President and his advisors, or between such advisors [(a)(5) of the PRA]
P-6 Release would constitute a clearly unwarranted invasion of personal privacy [(a)(6) of the PRA]

C. Closed in accordance with restrictions contained in donor's deed of gift.

PRM. Removed as a personal record misfile.

Freedom of Information Act - [5 U.S.C. 552(b)]

(b)(1) National security classified information [(b)(1) of the FOIA]
(b)(2) Release would disclose internal personnel rules and practices of an agency [(b)(2) of the FOIA]
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(b)(9) Release would disclose geological or geophysical information

Withdrawal/Redaction Sheet

(George Bush Library)

Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
04b. Biography	Biography of Otto Folin and Donald Van Slyke [personal information redacted] (3 pp.)		(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
Re-review Case #:		Appeal Disposition:	
P-2/P-5 Review Case #:		Disposition Date:	
AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

RESTRICTION CODES

Presidential Records Act - [44 U.S.C. 2204(a)]

P-1 National Security Classified Information [(a)(1) of the PRA]
P-2 Relating to the appointment to Federal office [(a)(2) of the PRA]
P-3 Release would violate a Federal statute [(a)(3) of the PRA]
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P-5 Release would disclose confidential advice between the President and his advisors, or between such advisors [(a)(5) of the PRA]
P-6 Release would constitute a clearly unwarranted invasion of personal privacy [(a)(6) of the PRA]

C. Closed in accordance with restrictions contained in donor's deed of gift.

PRM. Removed as a personal record misfile.

Freedom of Information Act - [5 U.S.C. 552(b)]

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(b)(8) Release would disclose information concerning the regulation of financial institutions [(b)(8) of the FOIA]
(b)(9) Release would disclose geological or geophysical information

"Document Control"

TYPE: ACTION DOCUMENT NUMBER: 9203498
ORIGINATOR: 02 STATUS I DIRECTORATE STATUS

FROM: WALLACE, Charles E.: LAMALIE AMROP INTERNATIONAL

TO: DR. D.A. BROMLEY

DATE OF
CORRESPONDENCE: 11/09/92

SUBJECT: HE IS WRITING TO SEEK DR. BROMLEY'S HELP IN FINDING
CANDIDATES FOR THE THE POSITION OF THE FIRST CEO FOR
THE AUSTRALIAN TECHNOLOGY GROUP.

DIRECTORATE STAFF
ASSIGNED: ALL ASSOCIATE DIRECTORS ASSIGNED:

ACTION STAFF
REQUIRED: COMMENTS TO DAB ACTION:

SENDER'S DUE DATE:
OSTP DUE DATE: 12/10/92 STAFF DUE DATE
DATE COMPLETED: DATE COMPLETED/DEPT:

COPIES TO:
D. Allan Bromley

WHITE HOUSE TRACKING #: CONTACT PERSON:
REMARKS: PHONE: EXT:

I don't have any candidates to suggest.



Eugene Wong

OSTP RECEIVED: 11/13/92 DEPT RECEIVED:
FILE: P-DAB-REFERRAL

CENTRAL FILES:



12/10

Charlie,

I don't know who
drafted the letter
or if DAB wrote
himself, but the
fund office sent it ~~the~~
up to me. so I've
closed out on C.T.

Erica

Document Originally
Attached to
Following Page

DEC 2 1992

"Document Control"

TYPE: ACTION
ORIGINATOR: 02

DOCUMENT NUMBER: 9203498
DIRECTORATE STATUS

FROM: WALLACE, Charles E.: LAMALIE AMROP INTERNATIONAL

TO: DR. D.A. BROMLEY

DATE OF
CORRESPONDENCE: 11/09/92

SUBJECT: HE IS WRITING TO SEEK DR. BROMLEY'S HELP IN FINDING
CANDIDATES FOR THE THE POSITION OF THE FIRST CEO FOR
THE AUSTRALIAN TECHNOLOGY GROUP.

DIRECTORATE
ASSIGNED: ALL ASSOCIATE DIRECTORS

STAFF
ASSIGNED:

*See lower
note file*

ACTION
REQUIRED: COMMENTS TO DAB

STAFF
ACTION:

SENDER'S DUE DATE:

OSTP DUE DATE: 12/10/92
DATE COMPLETED:

STAFF DUE DATE
DATE COMPLETED/DEPT: 12/8/92

COPIES TO: ALL ASSOCIATE DIRECTORS
D. Allan Bromley

WHITE HOUSE TRACKING #:

CONTACT PERSON:
PHONE:

EXT:

REMARKS:

*Allan - I believe the restrictions on
PAS's post-govt service rule out many
logical candidates for this. I can think
of none others. Karl*

OSTP RECEIVED: 11/13/92
FILE: P-DAB-REFERRAL

DEPT RECEIVED:

CENTRAL FILES:



"Document Control"

TYPE: ACTION DOCUMENT NUMBER: 9203498
ORIGINATOR: 02 STATUS I DIRECTORATE STATUS

FROM: WALLACE, Charles E.: LAMALIE AMROP INTERNATIONAL

TO: DR. D.A. BROMLEY

DATE OF
CORRESPONDENCE: 11/09/92

SUBJECT: HE IS WRITING TO SEEK DR. BROMLEY'S HELP IN FINDING
CANDIDATES FOR THE THE POSITION OF THE FIRST CEO FOR
THE AUSTRALIAN TECHNOLOGY GROUP.

DIRECTORATE STAFF
ASSIGNED: ALL ASSOCIATE DIRECTORS ASSIGNED:

ACTION STAFF
REQUIRED: COMMENTS TO DAB ACTION:

SENDER'S DUE DATE:

OSTP DUE DATE: 12/10/92 STAFF DUE DATE
DATE COMPLETED: DATE COMPLETED/DEPT:

COPIES TO:
D. Allan Bromley

WHITE HOUSE TRACKING #: CONTACT PERSON:
REMARKS: PHONE: EXT:

OSTP RECEIVED: 11/13/92 DEPT RECEIVED:
FILE: P-DAB-REFERRAL

CENTRAL FILES:



Withdrawal/Redaction Sheet

(George Bush Library)

Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
05a. Letter	To: Charles Wallace From: Allan Bromley Re: Response to request for help in finding candidates for a position [personal information redacted] (1 pp.)	12/9/92	(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
Re-review Case #:		Appeal Disposition:	
P-2/P-5 Review Case #:		Disposition Date:	
AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

RESTRICTION CODES

Presidential Records Act - [44 U.S.C. 2204(a)]

P-1 National Security Classified Information [(a)(1) of the PRA]
P-2 Relating to the appointment to Federal office [(a)(2) of the PRA]
P-3 Release would violate a Federal statute [(a)(3) of the PRA]
P-4 Release would disclose trade secrets or confidential commercial or financial information [(a)(4) of the PRA]
P-5 Release would disclose confidential advice between the President and his advisors, or between such advisors [(a)(5) of the PRA]
P-6 Release would constitute a clearly unwarranted invasion of personal privacy [(a)(6) of the PRA]

C. Closed in accordance with restrictions contained in donor's deed of gift.

PRM. Removed as a personal record misfile.

Freedom of Information Act - [5 U.S.C. 552(b)]

(b)(1) National security classified information [(b)(1) of the FOIA]
(b)(2) Release would disclose internal personnel rules and practices of an agency [(b)(2) of the FOIA]
(b)(3) Release would violate a Federal statute [(b)(3) of the FOIA]
(b)(4) Release would disclose trade secrets or confidential or financial information [(b)(4) of the FOIA]
(b)(6) Release would constitute a clearly unwarranted invasion of personal privacy [(b)(6) of the FOIA]
(b)(7) Release would disclose information compiled for law enforcement purposes [(b)(7) of the FOIA]
(b)(8) Release would disclose information concerning the regulation of financial institutions [(b)(8) of the FOIA]
(b)(9) Release would disclose geological or geophysical information

Withdrawal/Redaction Sheet

(George Bush Library)

Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
05b. Letter	To: Allan Bromley From: Charles Wallace Re: Request for help in finding candidates for a position [personal information redacted] (1 pp.)	11/9/92	(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
Re-review Case #:		Appeal Disposition:	
P-2/P-5 Review Case #:		Disposition Date:	
AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

RESTRICTION CODES

Presidential Records Act - [44 U.S.C. 2204(a)]

P-1 National Security Classified Information [(a)(1) of the PRA]
P-2 Relating to the appointment to Federal office [(a)(2) of the PRA]
P-3 Release would violate a Federal statute [(a)(3) of the PRA]
P-4 Release would disclose trade secrets or confidential commercial or financial information [(a)(4) of the PRA]
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C. Closed in accordance with restrictions contained in donor's deed of gift.

PRM. Removed as a personal record misfile.

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(b)(1) National security classified information [(b)(1) of the FOIA]
(b)(2) Release would disclose internal personnel rules and practices of an agency [(b)(2) of the FOIA]
(b)(3) Release would violate a Federal statute [(b)(3) of the FOIA]
(b)(4) Release would disclose trade secrets or confidential or financial information [(b)(4) of the FOIA]
(b)(6) Release would constitute a clearly unwarranted invasion of personal privacy [(b)(6) of the FOIA]
(b)(7) Release would disclose information compiled for law enforcement purposes [(b)(7) of the FOIA]
(b)(8) Release would disclose information concerning the regulation of financial institutions [(b)(8) of the FOIA]
(b)(9) Release would disclose geological or geophysical information

Withdrawal/Redaction Sheet

(George Bush Library)

Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
05c. Announcement	Job Description [personal information redacted] (1 pp.)		(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
Re-review Case #:		Appeal Disposition:	
P-2/P-5 Review Case #:		Disposition Date:	
AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

RESTRICTION CODES

Presidential Records Act - [44 U.S.C. 2204(a)]

P-1 National Security Classified Information [(a)(1) of the PRA]
 P-2 Relating to the appointment to Federal office [(a)(2) of the PRA]
 P-3 Release would violate a Federal statute [(a)(3) of the PRA]
 P-4 Release would disclose trade secrets or confidential commercial or financial information [(a)(4) of the PRA]
 P-5 Release would disclose confidential advice between the President and his advisors, or between such advisors [(a)(5) of the PRA]
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C. Closed in accordance with restrictions contained in donor's deed of gift.

PRM. Removed as a personal record misfile.

Freedom of Information Act - [5 U.S.C. 552(b)]

(b)(1) National security classified information [(b)(1) of the FOIA]
 (b)(2) Release would disclose internal personnel rules and practices of an agency [(b)(2) of the FOIA]
 (b)(3) Release would violate a Federal statute [(b)(3) of the FOIA]
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 (b)(6) Release would constitute a clearly unwarranted invasion of personal privacy [(b)(6) of the FOIA]
 (b)(7) Release would disclose information compiled for law enforcement purposes [(b)(7) of the FOIA]
 (b)(8) Release would disclose information concerning the regulation of financial institutions [(b)(8) of the FOIA]
 (b)(9) Release would disclose geological or geophysical information

TYPE: ACTION DOCUMENT NUMBER: 9203361
ORIGINATOR: 02 STATUS I DIRECTORATE STATUS

TO: DR. D.A. BROMLEY

SUBJECT: HE IS REQUESTING NOMINATIONS FOR THE FEDERAL ENVIRONMENTAL ENGINEER OF THE YEAR AWARD.

ACTION REQUIRED:	AS APPROPRIATE	STAFF ACTION:
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 SENDER'S DUE DATE: 01/16/93
 OSTP DUE DATE: 11/16/92 STAFF DUE DATE
 DATE COMPLETED: DATE COMPLETED/DEPT:

COPIES TO: ENVIRONMENT

WHITE HOUSE TRACKING #: CONTACT PERSON:  EXT:
REMARKS: PHONE:

DEPT RECEIVED:

CENTRAL FILES:

"Document Control"

TYPE: ACTION DOCUMENT NUMBER: 9203361
ORIGINATOR: 02-05 STATUS I DIRECTORATE STATUS C

FROM: HARMS, Timothy: THE CONFERENCE OF FEDERAL ENVIRONMENTAL ENGINEERS

TO: DR. D.A. BROMLEY

DATE OF
CORRESPONDENCE: 11/04/92

SUBJECT: HE IS REQUESTING NOMINATIONS FOR THE FEDERAL ENVIRONMENTAL ENGINEER OF THE YEAR AWARD.

DIRECTORATE STAFF
ASSIGNED: D. Allan Bromley ASSIGNED:

CB
Close out

ACTION STAFF
REQUIRED: AS APPROPRIATE ACTION:

SENDER'S DUE DATE: 01/16/93
OSTP DUE DATE: 11/16/92 STAFF DUE DATE
DATE COMPLETED: DATE COMPLETED/DEPT: 11/16/92

COPIES TO: ENVIRONMENT

WHITE HOUSE TRACKING #: CONTACT PERSON:
PHONE: EXT:
REMARKS: Reassigned to Karl Erb, 11/16/92

Allan - I do not believe there has been an environmental engineer on ASTP's personnel roster in recent years. Bill Busch would be close, but he was a detailee. If you want to nominate Bill, Nancy Maynard

OSTP RECEIVED: 11/04/92 DEPT RECEIVED:
FILE: P-DAB-REFERRAL

CENTRAL FILES: -- Bill's supervisor -- should be able to help.

11/16 Karl Erb ★

Withdrawal/Redaction Sheet

(George Bush Library)

Document No. and Type	Subject/Title of Document	Date	Restriction	Class.
06. Letter	To: Allan Bromley From: Timothy Harms Re: Request for nomination for Federal Environmental Engineer of the Year award [personal information redacted] (2 pp.)	10/30/92	(b)(6)	

Collection:

Record Group: Bush Presidential Records
Office: Science and Technology Policy, Office of (OSTP)
Series: Bromley, D. Allan, Files
Subseries: Correspondence Files
WHORM Cat.:
File Location: D. Allan Bromley: Referrals [2 of 7] [1992]

Date Closed:	1/11/2010	OA/ID Number:	62006-008
FOIA/SYS Case #:	2005-0336-F	Appeal Case #:	
Re-review Case #:		Appeal Disposition:	
P-2/P-5 Review Case #:		Disposition Date:	
AR Case #:		MR Case #:	
AR Disposition:		MR Disposition:	
AR Disposition Date:		MR Disposition Date:	

RESTRICTION CODES

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(b)(4) Release would disclose trade secrets or confidential or financial information [(b)(4) of the FOIA]
(b)(6) Release would constitute a clearly unwarranted invasion of personal privacy [(b)(6) of the FOIA]
(b)(7) Release would disclose information compiled for law enforcement purposes [(b)(7) of the FOIA]
(b)(8) Release would disclose information concerning the regulation of financial institutions [(b)(8) of the FOIA]
(b)(9) Release would disclose geological or geophysical information

CONFERENCE OF
FEDERAL ENVIRONMENTAL ENGINEERS

Nomination for
FEDERAL ENVIRONMENTAL ENGINEER
OF THE YEAR AWARD
1992

Agency making the nomination:_____

Agency point of contact:_____

Address:_____

Telephone Number:_____

NAME OF NOMINEE:_____

Position Title:_____

Organization and mailing address:_____

Telephone Number:_____

INITIAL QUALIFICATION OF THE NOMINEE

Only those who meet the following definition of an environmental engineer shall be eligible for the award. "An environmental engineer is defined as one who possesses a Baccalaureate or higher degree in engineering from a recognized college or university, or is licensed as an engineer by an official state licensing agency for professional engineers; or is classified in the Federal Service as an engineer and has prepared himself through additional study, training and experience in the sciences in combination with engineering, as applied to the control and improvement of the environment for the protection and promotion of health."

Nominee's Qualification (only one category required):

1. Name of College/University and Engineering Degree:

2. Professional Engineering License (give state and license number):

3. Present Job Classification in the Federal Service (If this is the only category used to qualify the nominee, provide a summary of training, education, or experience for the position):

- Position Title: _____

- Federal Service Occupational Code: _____

SELECTION CRITERIA

Environmental Contributions - limited to the last two years
(70 Percent)

The engineering of a system, process, or item of equipment characterized by initiative and imagination to an unusual degree which resulted in an advance of the art, a new application to environmental engineering, or which contributes significantly to the solution of an important and difficult problem; or

The development of a major improvement in a management procedure which increases efficiency, reduces cost, saves time, or otherwise contributes in large measure to the accomplishment of an important task; or

A record of achievement or sustained exemplary leadership in the management of environmental engineering programs.

Professional Prestige
(30 Percent)

Furnishes inspiration to and enhances the prestige of his or her professional colleagues.

Attach a maximum of four (4) pages of narrative for the nomination. Narrative is to be on 8.5" X 11" paper with not less than one inch margin on all sides and no more than 12 characters per inch.

Return completed nominations NO LATER THAN January 16, 1993 to:

Mr. Anthony Tesoriero
12203 Cedarbrook Lane
Laurel, Maryland 20708