

Machinations: Micro-PIXE Analysis in Mineralogy and Geochemistry

J. L. Campbell, W. J. Teesdale and N. M. Halden

Volume 19, Number 4, December 1992

URI: https://id.erudit.org/iderudit/geocan19_4fea01

[See table of contents](#)

Publisher(s)

The Geological Association of Canada

ISSN

0315-0941 (print)

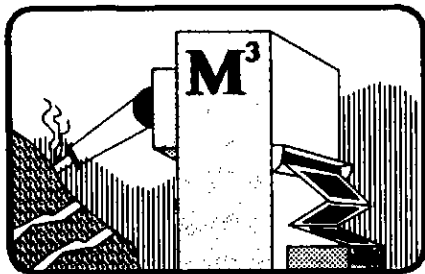
1911-4850 (digital)

[Explore this journal](#)

Cite this article

Campbell, J. L., Teesdale, W. J. & Halden, N. M. (1992). Machinations:: Micro-PIXE Analysis in Mineralogy and Geochemistry. *Geoscience Canada*, 19(4), 175–179.

Feature



Machinations

Micro-PIXE Analysis in Mineralogy and Geochemistry

J.L. Campbell and W.J. Teesdale
Physics Department
University of Guelph
Guelph, Ontario N1G 2W1

N.M. Halden
Department of Geological Sciences
University of Manitoba
Winnipeg, Manitoba R3T 2N2

INTRODUCTION

Proton-induced X-ray emission (PIXE) has been used as an analytical tool for 20 years. In its microbeam version (micro-PIXE), it is a close analogue of the long-established electron microprobe, since in both instruments a focussed beam of charged particles excites characteristic X-rays in a specimen and, in both cases, these may then be registered by energy-dispersive spectroscopy. Electron probe micro-analysis (EPMA) has been a workhorse of geochemistry, using both energy- and wavelength-dispersive X-ray spectroscopy. With equivalent spatial resolution and with limits of detection that are often markedly superior to those of EPMA, micro-PIXE is proving to be of increasing use in the field, providing quantitative trace element analysis as well as the ability to map trace element distributions (Watt and Grime, 1987).

This article describes the Scanning Proton

Microprobe (SPM) at the University of Guelph, which is used by a growing number of North American geochemists and mineralogists from various institutions. It concentrates on the practical aspects, since the physics of proton-induced X-ray emission are simple and well known, and are discussed in depth elsewhere (Johansson and Campbell, 1988). The Guelph instrument is similar to various other proton microprobes around the world, but is one of a handful that were designed specifically for analysis of specimens from the earth sciences. During three years of operation, many thousands of spot analyses have been conducted on a variety of sample types, and considerable practical experience amassed (Campbell *et al.*, 1990). Facilities for beam scanning and element mapping were added during 1991, and new applications of these are currently being explored.

PROTON MICROBEAM

As in most proton microprobes, the beam is provided by a small Van de Graaff accelerator, which the authors customarily operate at 3 MeV energy. In EPMA, beam focussing is done with small electrostatic lenses of cylindrical symmetry, but, in micro-PIXE, the much higher magnetic rigidity of 3 MeV protons demands the use of electric or magnetic quadrupole lenses. The beam is magnetically steered onto a small aperture which acts as the object for the demagnifying lens system. This object aperture is formed by a set of four water-cooled tantalum jaws mounted on micrometer drives, and its dimensions are typically 40×160 μm. A doublet of magnetic quadrupoles then focusses the beam to a spot size of typically 5×5 μm at the specimen. A vacuum better than 10⁻⁶ mm Hg is necessary in the beam transport system to prevent beam broadening by scatter on residual gas molecules.

Beam spots as small as 0.5×0.5 μm have been reported (Grime *et al.*, 1991), containing sufficient current to conduct micro-PIXE. However, beamspots of 5-30 μm tend to be preferred in geochemical work. For analysis of individual grains, the larger beam diameter better resembles the depth probed (tens of microns) and provides a degree of averaging over the volume sampled. In addition, broader beams minimize the localized thermal

stress which can cause cracking at high current densities. A feature of the Guelph SPM that is infrequently found on proton microprobes is an on-demand beam deflector; each time the detection system (see below) registers an X-ray from the specimen, the beam is deflected off the specimen and is returned only when the electronics have finished processing the information. This eliminates unnecessary heating of the specimen and reduces damage.

En route from the focussing lens to the specimen, the beam passes between two pairs of small plates connected to sawtooth voltage supplies which are under computer control. This enables rastering of the beam over desired areas of a specimen for the purpose of imaging the distribution of elements.

SPECIMENS

Analytical samples and their preparation are essentially as for EPMA. A large number of grains or small mineral specimens can be potted in epoxy, polished and carbon-coated (a conducting path is necessary for beam current removal and measurement). The typical one-inch diameter mounts used in EPMA work are perfectly compatible, and four of these, attached to the various faces of the sample-holder, provide a full day's work, with no need to open the specimen chamber during the day. The greater penetration of protons (tens of microns) as opposed to electrons (microns) demands that individual grains be thick enough (50 μm, typically) to stop the beam; it is usually obvious from the X-ray spectrum if the beam has penetrated to a second grain of different species or to the substrate.

Geological thin sections as prepared for EPMA are also well suited for micro-PIXE. Thicknesses of 50-100 μm are preferable to the usual 30 μm; otherwise, X-rays of elements in the glass backing (e.g., barium) may appear in the spectrum.

The authors' experience is that micro-PIXE is essentially non-destructive. A 10 nA current in a 10×10 μm spot for 15 minutes has not resulted in any visible damage to the mineral samples analysed to date, including carbonates and phosphates, nor have ensuing changes in trace element concentrations been observed. This is particularly advan-

tageous when point analyses are done in conjunction with 2-D imaging of element distribution. The analyst can locate the proton beam for point analysis with the aid of an X-ray map of the region or feature of interest. The light brown hydrocarbon stain left by the beam is a useful record of the impact point.

SPECIMEN CHAMBER

Microprobe specimen chambers share a common vacuum with the beam transport line. Specimen motion is provided by an XYZ stage, which, in the authors' case, is driven by external stepping motors. The Si(Li) detector should have a large area and be as near the specimen as possible in order to maximize recorded X-ray intensity and so minimize analysis time or optimize detection limits. The authors use an 80 mm² Link Analytical detector positioned to subtend a solid angle slightly more than 0.08 sr. A 30 mm² detector with a thinner window (8 μm versus 25 μm) may be substituted to extend the low atomic number cut-off from aluminum down to sodium. The presence in the spectrum of the X-rays of all elements present above the limit of detection (LOD) means that only one measurement is needed. Wavelength-dispersive spectroscopy, with its superior detection efficiency, is precluded by its low geometric efficiency.

For geological work, a high-power microscope is mandatory, since individual grains must be viewed with resolving power of a very few microns. Only a few of the existing SPMs have sufficiently sophisticated optics for professional geological work. The Guelph SPM uses the optical system of a defunct Etek electron probe, providing both illumination and viewing along the specimen normal with magnification of 60, 150 or 300. The microscope is fitted with a CCTV camera, and the image of the specimen is presented on a colour monitor. The 90° viewing angle, unconventional in micro-PIXE, demands that the proton beam enter the specimen at 45° to the normal; the X-ray take-off angle is 45°. Illumination from the rear is provided for thin specimens.

To ensure that charge measurement is not rendered inaccurate by loss of secondary electrons, these are returned to the target by the electric field of a suppressor grid in front of the target. Secondary electrons can be monitored by turning off the suppressor and utilizing a channeltron, which is useful in mapping applications.

Many applications involve the measurement of high atomic number trace elements in a low-Z matrix; silver in sulphide minerals such as ZnS is a good example. In such work, an absorbing foil is needed be-

tween specimen and detector to attenuate the dominant X-rays of the major element and, consequently, their pile-up peaks, while transmitting most of the higher-energy X-rays of the trace elements. A selection of aluminum and Mylar foils is carried on a vertical ladder between specimen and detector.

The chamber instrumentation and the data acquisition are controlled by locally written software, resident on a 80386-type microcomputer. The specimen is moved by cursors or by a joystick, filter commands select the required absorbing foil, and microscope commands rotate the appropriate objective to provide the desired optical magnification. The beam charge, digitized by a current integrator, is read by the computer, which also records and stores the X-ray spectrum generated by the Si(Li) detector. During preliminary optical inspection, the coordinates of points to be analysed are stored, and the computer then oversees analysis of the specimen suite without operator intervention.

X-RAY SPECTRUM PROCESSING AND STANDARDIZATION IN SPOT ANALYSIS

The Si(Li) spectra are more complex than in EPMA, since trace elements contribute, in addition to the major and minor constituents.

Table 1 Some representative limits of detection using a Si(Li) detector whose solid angle is 0.08 sr.

Mineral	Filter (μm)	Time (min)	Charge (μC)	Current (nA)	Rate (c/s)	Beam Spot ($\mu\text{m} \times \mu\text{m}$)	LOD (ppm)
Quartz	106	5	5	16	1500	10 \times 14	Ni 1.1 Zn 0.9 Se 0.6 Au 2.6
	249	15	7	7	770	10 \times 14	Ni 5.4 Pd 2.6 Ag 3.2
Garnet	106	5	1	3	5000	10 \times 10	Ni 4.6 Zn 2.7 Se 2.7 Ru 6.8
Pentlandite	350	5	4.8	15	4300	5 \times 10	Se 6 Mo 4.3 Pd 4.5 Ag 6.3
Calcite	106	5	1.25	4.1	90	10 \times 10	Fe 10 As 2.0 Sr 1.8
Apatite	21	15	0.34	0.37	4500	5 \times 5	Fe 13 Sr 5.2 Y 5.4 Sm 110 Yb 36 Th 13
Titanite	106	5	1.8	5.8	2880	10 \times 10	Sr 2.9 Y 3.5 Zr 9.1 Nb 11.3 Th 8.2

Since the problems of separating overlapping peaks from one another and from a continuous background are essentially the same as in EPMA, it is not surprising that spectrum treatment approaches are similar. Several available software packages offer considerable sophistication. All of these build a spectrum model from an accurately known (Maxwell *et al.*, 1989; Ryan *et al.*, 1990) atomic physics data base, and adjust this to fit the measured spectrum, using least-squares procedures. Some software packages model the background continuum, while others remove it mathematically. Carrying out the appropriate matrix corrections,

these codes then convert the fitted X-ray intensities to element concentrations. This step may involve measurement of standards, or concentrations may sometimes be derived relative to a major element of known concentration in the specimen. EPMA and micro-PIXE are often used in complementary fashion (Remond *et al.*, 1987); EPMA provides the major and minor concentrations, which are then used in both the matrix correction and the standardization steps by the PIXE software to generate trace element concentrations.

At Guelph, the authors prefer to use a set of synthetic sulphide mineral standards gen-

erously provided by L.J. Cabri. These contain various trace elements in pyrrhotite, sphalerite and chalcopyrite hosts, and results obtained with them have been in good agreement with EPMA data, where concentrations were high enough that a comparison of the two techniques was possible (Remond *et al.*, 1987).

The on-demand beam deflector confers further advantages. First, there is no necessity for dead time corrections. In addition, the incidence of pile-up events in the spectrum is greatly reduced.

The Guelph PIXE software package, GUPIX (Maxwell *et al.*, 1989), which is widely

Table 2 Some applications of micro-PIXE in the earth sciences.

Sample	Elements	Comments	Instrument	References
Sulphide minerals	Ag	Chalcopyrite confirmed as Ag carrier	Heidelberg	Harris <i>et al.</i> (1984)
Sulphide minerals	Ge, As, Se, Ag, Cd, In, Sn, Pb	Chalcopyrite, sphalerite Ag carriers	Heidelberg	Cabri, Blank <i>et al.</i> (1985)
Sulphide minerals	PGEs, Se, Zn, Ag	High PGE in Stillwater pentlandites, none in Sudbury	Heidelberg	Cabri, Campbell <i>et al.</i> (1985)
Sulphide minerals	PGEs, Se, Ti, Ag, Cd, Zn, Ga, Ge	Equal Se partitioning	Guelph	Paktunc <i>et al.</i> (1990)
Sulphide minerals	PGEs	Extensive study of the Noril'sk deposit; Pd correlates to Ni/Fe in pentlandite	Guelph	Czamanske <i>et al.</i> (1992)
Garnet	Zr, Y, Ga, Ge, Sr, Ni, Mn	Spot analyses along grain diameters	Sydney	Smith <i>et al.</i> (1991)
Garnets	Fe, Ti, Zr, Y, Cr, Ni, Ga	Trace element zoning parallels that of major and minor elements	Sydney	Griffin, Smith <i>et al.</i> (1989)
Inclusions in diamond	Mn, Ni, Cu, Zn, Ga, Pb, Rb, Sr, Y, Zr, Nb, Ta, Ba, Mo	Significant disequilibrium between different grains of the same mineral	Sydney	Griffin <i>et al.</i> (1988)
Garnet and olivine	Ni	Ni partitioning as a geothermometer, pertinent to diamond exploration	Sydney	Griffin, Cousens <i>et al.</i> (1989)
Garnet and clinopyroxene	Nb, Ta, Zr, Sr, Y	Partitioning of Nb and Ta	Sydney	Green <i>et al.</i> (1989)
Olivine, orthopyroxene, clinopyroxene, phlogopite, amphibole and apatite	HFSE, LIL and REE	Partitioning of elements between minerals in metasomatized mantle rocks	Sydney	O'Reilly <i>et al.</i> (1991)
Zircons	Pb, Ti, Hf, Zr, U	Distributions across single grains	Harwell, U.K.	Clark <i>et al.</i> (1979)
Lunar rocks from Apollo 14, 15 and 17	Zr, Nb	Partitioning studies by step scans of ilmenite, ulvospinel and armalcolite	Heidelberg	Blank <i>et al.</i> (1982) Blank <i>et al.</i> (1984)
Iron meteorites	Cu, Ni	Partitioning between troilite and metal	Brookhaven	Sutton <i>et al.</i> (1987)
Apatite	REE	Cathodoluminescence and rare element study	Kingston	Roeder <i>et al.</i> (1987)
Chondritic meteorites	Ni to Ru	PIXE confirmed smooth variations of abundances	Los Alamos	Burnett <i>et al.</i> (1989)
Fluid inclusions in quartz and pegmatite	K, Ti, Mn, Fe, Cu	Light elements (e.g., F, Na, Al) by gamma emission; proton energy >3.5 MeV	Kingston	Anderson <i>et al.</i> (1989)
Shergotty meteorite	REE	Test if radiogenic U/Pb ratio is disturbed	Los Alamos	Jones <i>et al.</i> (1985)
Allende meteorite	C, O, Si, S, Ca, Fe	Glass inclusions	Amsterdam	Heymann <i>et al.</i> (1988) Makjanic <i>et al.</i> (1989)

used, runs on an 80836 microcomputer. Spectrum processing time is generally less than the time needed to acquire the spectrum, which facilitates decision-making during analysis of large sample suites.

LIMITS OF DETECTION IN SPOT ANALYSIS

Limits of Detection (LODs) are dictated by the ratio of peak intensity to the statistical variation in the underlying spectrum background against which a peak must be discerned. Since, from Poisson statistics, that variation is proportional to the square root of background intensity, the LOD decreases in proportion to the square root of any factor that increases overall spectrum intensity. In principle then, LODs may be improved by increased beam current, but a concomitant increase in spot size may then be necessary to ensure that thermal stress remains tolerable. There is little possibility at Guelph of an improvement *via* increased efficiency of X-ray detection, since this is already large. With the spot size and beam current optimized, and the appropriate absorber chosen, an increase in measurement time is the remaining route to lower LODs.

While the LODs are, in principle, predictable, calculations can be rendered irrelevant both by interference of neighbouring X-ray peaks and by the presence of small concentrations of elements (e.g., Al, F, Na) which emit gamma rays under proton bombardment, thus increasing the spectrum background. The authors' practice is to simply run each new specimen type and determine the practical LODs. Some examples are shown in Table 1. With silicates in which no major elements contribute X-rays to the spectrum in the energy region occupied by the X-rays of the trace element of interest, LODs at the ppm level are obtained in the typical counting times of a few minutes; the presence of some 10% by mass of transition metals (garnets) worsens the LODs a little. With sulphide minerals, where K X-rays of Fe, Cu, Ni or Zn dominate the spectrum, LODs increase to, typically, a few ppm for elements such as Se, Pd, Rh and Ag. In the garnet example, the beam current could be increased significantly, but the electronic system is already operating at its maximum throughput. It could only cope with an increase in counting rate if its time-constants were markedly reduced to generate shorter pulses, a manoeuvre that results in significant worsening of energy resolution. The LOD issue is clearly a complex one, in which practical experience is important.

ACCURACY OF QUANTITATIVE ANALYSIS

Many publications, including some in the application list presented in Table 2, have demonstrated good agreement between EPMA and micro-PIXE analysis of specimens containing trace element concentra-

tions well above the typical EPMA LOD of a few hundred ppm. Problems arise in micro-PIXE analysis of standard reference materials, since these are rarely homogeneous on the scale sampled by the microbeam. Ryan *et al.* (1990) fused the United States Geological Survey rock standards BCR-1, AGV-1 and GSP-1 to form glasses, and tested homogeneity using EPMA. For BCR-1, the ratio of the concentrations measured by micro-PIXE to the accepted values for 14 trace elements was within 1% of unity. Good agreement resulted also for AGV-1 (although there was evidence of heterogeneity), while in GSP-1 the heterogeneity was marked. While this work demonstrates that PIXE is quantitative at concentrations down to a few ppm, it also highlights the problems inherent in the use of conventional standard materials. This is why the authors currently use synthetic standards with demonstrated homogeneity (Campbell *et al.*, 1990). Much work remains to be done in the field of cross-analysing mineral standards between micro-PIXE and EPMA.

APPLICATIONS OF MICRO-PIXE

Table 2 presents an overview of some of the published applications to a variety of geological problems. Space limitations preclude an exhaustive list. Work with conventional broad-beam PIXE is not included; naturally, the considerable volume of commercial analyses done at Guelph and Sydney is not included. The authors do not imply that the list of micro-PIXE studies is complete; nor does it cover the development and demonstration work which appears mainly in the analytical physics literature, and in various conference proceedings that focus on techniques. Rather, Table 2 selects various well-defined earth science investigations that have been reported in the geological literature. Of particular interest in Canada is the pioneering work of L.J. Cabri on sulphide minerals, first using the Heidelberg microprobe, and subsequently using the authors' instrument at Guelph. A considerable body of work on zoning phenomena and on diamond-bearing minerals has been produced at the Sydney facility. The microprobes at Los Alamos, Heidelberg and Amsterdam have concentrated on extra-terrestrial specimens.

Almost all of the reported work comprises quantitative spot analysis of mineral species, and much of it involves the complementary use of EPMA and micro-PIXE. In zoning studies, spot sequences across crystal diameters (e.g., zircons and garnets) are frequently used. Very little of this work, to date, involves dynamic elemental imaging with scanning microbeams, although elegant early demonstrations of the potential of this technique exist; an example is the work of Fraser *et al.* (1984), which showed that Sr was confined to cracks and grain boundaries in matasomatized garnet lherzolite xenoliths. More recently, Fraser *et al.* (1989) ex-

amined Mn, Zn and Sr variations in zoned carbonate cements, providing useful chemostratigraphic information.

SUMMARY

Micro-PIXE is an established quantitative technique whose detection limits can be as low as a few ppm in point analysis mode, and which, in scanning mode, can provide one- and two-dimensional distributions of minor and even trace elements for zoned minerals. The Guelph instrument and counterparts at Heidelberg, Amsterdam, Oxford, Sydney and Los Alamos are being used increasingly by mineralogists and geochemists. The full potential of the technique is far from realized.

REFERENCES

- Anderson, A.J., Clark, A.H., Ma, X.-P., Palmer, G.R., MacArthur, J.D. and Roedder, E., 1989, Proton-induced X ray and gamma ray emission analysis of unopened fluid inclusions: *Economic Geology*, v. 84, p. 924-939.
- Blank, H., Nobiling, R., Traxel, K. and El Goresy, A., 1982, Quantitative proton microprobe trace element analysis of co-existing opaque oxides in lunar rocks and their genetic implications: *Lunar and Planetary Science*, v. 13, p. 49-50.
- Blank, H., El Goresy, A., Janicke, J., Nobiling, R. and Traxel, K., 1984, Partitioning of Zr and Nb between co-existing phases in lunar rocks determined by quantitative microprobe analysis: *Earth and Planetary Science Letters*, v. 68, p. 19-33.
- Burnett, D.S., Woolum, D.S., Benjamin, T.M., Rogers, P.S.Z., Duffy, C.J. and Maggiore, C., 1989, A test of the smoothness of the distribution of elemental abundances of carbonaceous chondrites: *Geochimica et Cosmochimica Acta*, v. 53, p. 471-481.
- Cabri, L.J., Blank, H., El Goresy, A., Laflamme, J.H.G., Nobiling, R., Sizgosc, M.B. and Traxel, K., 1985, Quantitative trace element analysis of sulfides from Sudbury and Stillwater by proton microprobe: *The Canadian Mineralogist*, v. 23, p. 521-542.
- Cabri, L.J., Campbell, J.L., Laflamme, J.H.G., Leigh, R.G., Maxwell, J.A. and Scott, J.D., 1985, Proton microprobe analysis of trace elements in sulfides from some massive sulfide deposits: *The Canadian Mineralogist*, v. 23, p. 133-148.
- Campbell, J.L., Maxwell, J.A., Teesdale, W.J., Wang, J.-X. and Cabri, L.J., 1990, Micro-PIXE as a complement to electron probe microanalysis in mineralogy: *Nuclear Instruments and Methods in Physics Research*, v. B44, p. 347-356.
- Clark, J.G., Gulson, B.L. and Cookson, J.A., 1979, Pb, U, Ti, Hf and Zr distribution in zircons determined by proton microprobe and fission track techniques: *Geochimica et Cosmochimica Acta*, v. 43, p. 905-918.
- Czamanske, G.K., Kunitov, V.E., Cabri, L.J., Zientek, M.L., Calk, L.C. and Likhachev, A.P., 1992, A proton microprobe study of sulfide ores from the Noril'sk-Talnakh district, Siberia: *The Canadian Mineralogist*, v. 30, p. 249-287.
- Fraser, D.G., Watt, F., Grime, G.W. and Takacs, J., 1984, Direct determination of strontium enrichment on grain boundaries in a garnet lherzolite xenolith by proton microprobe analysis: *Nature*, v. 312, p. 352-354.

- Fraser, D.G., Feltham, D. and Whiteman, M., 1989, High resolution scanning proton microprobe studies of micron-scale zoning in a secondary dolomite: implications for studies of redox behaviour in dolomites: *Sedimentary Geology*, v. 65, p. 223-232.
- Green, T.H., Sie, S.H., Ryan, C.G. and Cousens, D.R., 1989, Proton microprobe-determined partitioning of Nb, Ta, Zr, Sr and Y between garnet, clinopyroxene and basaltic magma at high pressure and temperature: *Chemical Geology*, v. 74, p. 201-216.
- Griffin, W.L., Jaques, A.L., Sie, S.H., Ryan, C.G., Cousens, D.R. and Suter, G.F., 1988, Conditions of diamond growth: a proton microprobe study of inclusions in West Australian diamonds: *Contributions to Mineralogy and Petrology*, v. 99, p. 143-158.
- Griffin, W.L., Smith, D., Boyd, F.R., Cousens, D.R., Ryan, C.G., Sie, S.H. and Suter, G.F., 1989, Trace-element zoning in garnets from sheared mantle xenoliths: *Geochimica et Cosmochimica Acta*, v. 53, p. 561-567.
- Griffin, W.L., Cousens, D.R., Ryan, C.G., Sie, S.H. and Suter, G.F., 1989, Nickel in chrome pyrope garnets: a new geothermometer: *Contributions to Mineralogy and Petrology*, v. 103, p. 199-202.
- Grime, G.W., Dawson, M., Marsh, M., MacArthur, I.C. and Watt, F., 1991, The Oxford submicron nuclear microscopy facility: *Nuclear Instruments and Methods in Physics Research*, v. B54, p. 52-63.
- Harris, D.C., Cabri, L.J. and Nobile, R., 1984, Silver-bearing chalcopyrite, a principal source of silver in the Izok Lake massive sulfide deposits: confirmation by electron-and proton-microprobe analyses: *The Canadian Mineralogist*, v. 22, p. 493-498.
- Heymann, D., Makjanic, J., Van der Stap, C.C.A.H., Vis, R.D. and Verheul, H., 1988, Carbon, oxygen, silicon, sulfur, calcium and iron determinations in 24 dark clasts and one dark inclusion of the Allende meteorite by $^{12}\text{C}(d,p)^{13}\text{C}$ nuclear reaction and PIXE: *Meteoritics*, v. 23, p. 131-137.
- Johansson, S.A.E. and Campbell, J.L., 1988, PIXE: A Novel Technique for Elemental Analysis: John Wiley and Sons Ltd., Chichester, U.K.
- Jones, J.H., Benjamin, T.M., Duffy, C.J., Rogers, P.S.Z., Hollander, M. and Maggiore, C., 1985, A tale of two phosphate-REE reservoirs in the Shergotty meteorite: *Meteoritics*, v. 20, p. 674-675.
- Makjanic, J., Touret, J.L.R., Vis, R.D. and Verheul, H., 1989, Carbon in glass inclusions in the Allende meteorite: *Meteoritics*, v. 24, p. 49-55.
- Maxwell, J.A., Campbell, J.L. and Teesdale, W.J., 1989, The Guelph PIXE software package: *Nuclear Instruments and Methods in Physics Research*, v. B43, p. 218-230.
- Paktunc, A.D., Hulbert, L.J. and Harris, D.C., 1990, Partitioning of the platinum-group and other trace elements in sulfides from the Bushveld Complex and Canadian occurrences of nickel-copper sulfides: *The Canadian Mineralogist*, v. 28, p. 475-488.
- O'Reilly, S.Y., Griffin, W.L. and Ryan, C.G., 1991, Residence of trace elements in metasomatized spinel/hercynite xenoliths: a proton microprobe study: *Contributions to Mineralogy and Petrology*, v. 109, p. 98-113.
- Remond, G., Cesbron, F., Traxel, K., Campbell, J.L. and Cabri, L.J., 1987, Electron microprobe analysis and proton-induced X ray spectrometry applied to trace element analysis in sulfides: *Scanning Microscopy*, v. 1, p. 1017-1037.
- Roeder, P.L., MacArthur, J.D., Ma, X.-P., Palmer, G.R. and Mariano, A.N., 1987, Cathodoluminescence and microprobe study of rare-earth elements in apatite: *American Mineralogist*, v. 72, p. 801-811.
- Ryan, C.G., Cousens, D.R., Sie, S.H., Griffin, W.L. and Suter, G.F., 1990, Quantitative PIXE microanalysis of geological material using the CSIRO proton microprobe: *Nuclear Instruments and Methods in Physics Research*, v. B47, p. 55-71.
- Smith, D., Griffin, W.L., Ryan, C.G. and Sie, S.H., 1991, Trace element zonation in garnets from the Thumb: heating and melt infiltration below the Colorado plateau: *Contributions to Mineralogy and Petrology*, v. 107, p. 60-79.
- Sutton S.R., Delaney, J.S., Smith, J.V. and Prinz, M., 1987, Copper and nickel partitioning in iron meteorites: *Geochimica et Cosmochimica Acta*, v. 51, p. 2653-2662.
- Watt, F. and Grime, G.W., 1987, Principles and applications of high-energy ion microbeams: Adam Hilger, Bristol, U.K.

Accepted, as revised, 24 May 1992.